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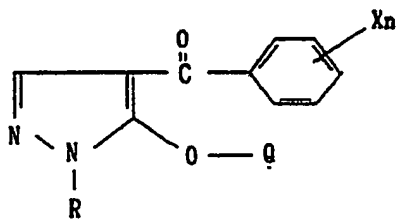
(54) **Herbicidal 4-benzoyl-1-alkyl(alkenyl)-pyrazoles.**

(57) Novel pyrazole derivatives of the formula I:



(I)

EP 0 203 428 A1

MUST exclude

or already excluded?

wherein

R represents a lower alkyl group or a lower alkenyl group atoms which may be substituted by halogen atom,

X represents a halogen atom, a lower alkyl group, nitro group, cyano group, a lower alkylsulfonyl group or trifluoromethyl group,

n is an integer of 2 to 4,

Q represents hydrogen atom; an aralkyl group which may be substituted by halogen atom, nitro group, cyano group or a lower alkyl group; benzenesulfonyl group which may be substituted by a lower alkyl group or halogen atom; benzoyl group which may be substituted by a lower alkyl group or halogen atom; phenacyl group which may be substituted by a lower alkyl group or halogen atom; a lower alkyl group which may be substituted by halogen atom;

a lower alkenyl group which may be substituted by halogen atom; or a lower alkynyl group,

and a method for preparation of said derivatives, a selective berbicidal composition containing said derivatives as active ingredient,

as well as a method for controlling weeds using said derivatives.

HERBICIDAL 4-BENZOYL-1-ALKYL (ALKENYL) -PYRAZOLES

BACKGROUND OF THE INVENTION

(1) Field of the Invention

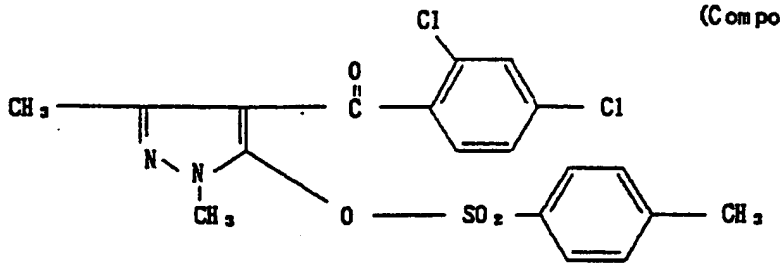
This invention relates to novel pyrazole derivatives, method for preparation thereof, a selective herbicidal composition containing as an active ingredient one or more of said derivatives, and method for damaging and controlling weeds using said derivatives.

(2) Description of the Prior Art

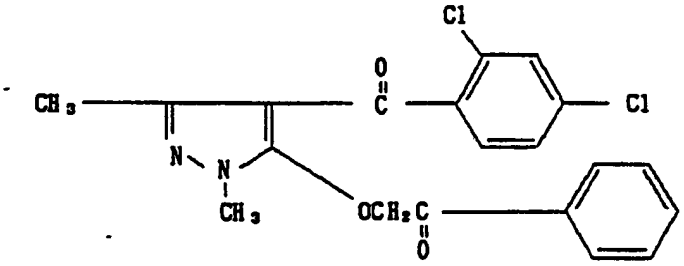
Hitherto, some pyrazole derivatives having herbicidal activity has been known. For example, Japanese Patent Publication No. 36648/79 (corresponding to U.S. Pat. Nos. 4,063,925 and 4,146,726) and Japanese Laid-open Patent Publication No. 41872/79 (corresponding to U.S. Pat. No. 4,230,481), Japanese Laid-open Patent Publication No. Sho 56-61358 (61358/81), U.S. Pat. No. 4,557,753 and U.S. Pat. Appln. No. 735,656 disclose certain 4-benzoyl derivatives of pyrazole which are useful for herbicides.

Among these pyrazole derivatives, however, two compounds represented by the formula below are used practically and commercially as an active ingredient of a herbicide for use in a paddy field as far as the present inventors' knowledge is concerned.

(Compound A)



(Compound B)

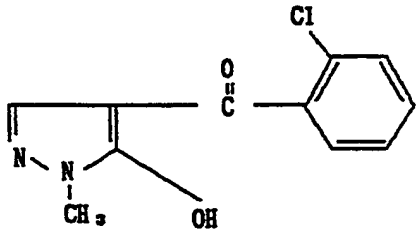


All the pyrazole derivatives disclosed by the above-mentioned publication No. 41872/79 have a lower alkyl group, specifically CH_3 group, at 3-position of the pyrazole ring.

Also the majority of the pyrazole derivatives disclosed by the above-mentioned publication No. 36648/79 have a lower alkyl group at th 3-position of the pyrazole ring and —OH, —SH, a salt thereof or an organic acid

ester thereof at 5-position of said ring; among the pyrazole derivatives disclosed by said publication, only the compound of the following formula is exemplified as a pyrazole derivative having hydrogen atom at 3-position (i.e., unsubstituted at 3-position) of the pyrazole ring:

(Compound C)



The compound C, however, is inferior to the commercialized compound A in herbicidal activity as is apparent from the biological test data given in the above-mentioned publication No. 38648/79.

Despite the fact that a number of pyrazole derivatives have been synthesized and the herbicidal activity thereof has been tested, there has not been found a pyrazole derivative which is unsubstituted at 3-position of the pyrazole ring and which exhibits herbicidal activity except the above-mentioned compound C.

This is because synthesis of pyrazole derivatives unsubstituted at 3-position has been very difficult while a pyrazole derivative substituted by an alkyl at 3-position has been relatively readily prepared, and because the former compound has been believed to be less active in herbicidal action and thus less practical than the latter one.

The present inventors have done intensive researches on pyrazole derivatives having hydrogen atom at 3-position of the pyrazole ring and have unexpectedly found that some of these pyrazole derivatives exhibit herbicidal action against a wide range of weeds, particularly against perennial weeds such as perennial flat sedge (Cyperus serotinus), bulrush (Scirpus juncoides) and perennial spikerush (Eleocharis kuroguwai) which have been difficult to control and against which no useful herbicide has been developed. Moreover, the present inventors have found a process for readily preparing such 3-H pyrazole derivatives to complete the present invention. The 3-H pyrazole derivatives have no phytotoxicity upon a paddy-rice plant and, thus, can be used with safety.

The present inventors have filed an application for an invention on the basis of the above-mentioned knowledge and have granted a patent thereto under the U.S. Patent No. 4,557,753,. In this U.S. Patent No. 4,557,753, the pyrazole derivatives have hydrogen atom at 3-position of pyrazole ring, CH_3 group at 1-position thereof and specific group is substituted at 5-position thereof.

After the present inventors have intensively advanced the researches, they have found that in the above-mentioned 3-H pyrazole derivatives, when 1-C_2H_5 compounds having an ethyl group at 1-position of pyrazole ring and 1-CH_3 compounds having methyl group at the same position are compared, 1-C_2H_5 compounds showed remarkable effects to the grass weeds, and the improvement of the effects to the paddy weeds such as Monochoria vaginalis, Alisma canaliculatum has reached to more than ten times as the effects of 1-CH_3 compounds, which has been way above the initial expectation.

Among the compounds according to th present invention, there exist some compounds which show superior as to safety to cultivated plants, e.g., rice (Oryza satva), or show very high safety to corn (Zea mays) in the dry field farming, while some compounds show remarkable improvement of the effects to grass weeds in the field of corn (Zea mays), yellow nutsedges (Cyperus esculeutus) and broadleaf-weeds in comparison with that of 1-CH_3 compounds.

Moreover, in comparison with prior arts, the specificity of substitution at 1-position of pyrazole ring which is the features f the present invention is summed up as follows:

Firstly, in case of 3-CH_3 type pyrazoles as recognized in the earli r patent application, U.S. Pat. No. 4,063,925, and as apparent from the comparison between the compounds of said U.S. Patent No. 4,063,925: Compounds No. 44 and No. 11, Compounds No. 107 and No. 51, Compounds No. 108 and No. 14, and Compounds No. 109 and No. 105, it is clear that the intention of said U.S. Patent No. 4,063,925 was directed to 1-CH_3 compounds because there was no remarkable difference of activity between 1-CH_3 type pyrazoles and pyrazoles substituted by alkyl group having more than two carbon atoms at 1-position (under the both conditions of paddy field and dry field farming).

On the other hand, in case of 3-H type pyrazoles, as shown in the later-described tables, there was remarkable difference of activity between 1-CH_3 compounds and pyrazoles substituted by alkyl group having more than two carbon atoms at 1-position. In this as pect, it is understood that even a person skilled in the art could not expect the present invention.

Especially, under not only paddy-rice field conditions but also dry field farming, the present invention has such an inventive step that the present invention shows remarkable higher activity in not only soil treatment but also foliage application which show very high cultivated plant-selectivity. Furthermore, the present invention has sufficient inventive step in a point that it shows higher activity with respect to seriously harmful weeds such as grass weeds, broadleaf-weeds, etc., and further to Cyperus esculeutus, yellow nutsedge. Also, Japanese Laid-open Patent Publication No. Sho 56-61358 (61358/81), one of the prior arts, shows herbicidal activity of pyrazoles having methyl group at 3-position under the paddy-field conditions. In said Japanese Laid-open Patent Publication, the compound No. 4 has isopropyl group at 1-position. However, comparing with the compounds No. 2, No. 3 and No. 5, all having methyl group at 1-position, said compound No. 4 has lower activity. As aforementioned, in the 3-methyl type pyrazoles, the substituent of more than 1-C_2 has no superior properties in comparison with 1-methyl compounds. Thus, it shows that the fact that in 3-H type pyrazoles, the substitu nt having more than C_2 at 1-position is superior to methyl group could not be expected. At the same time, in said Japanese Laid-open Patent Publication, only applicability to the rice-field conditions was described. Therefore, the safety of the present compounds to economic plants, corn (Zea mays) included and applica bility of the present compounds to the dry-field farming can not be expected from said Japanese Laid-open Patent Publication.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a novel pyrazole derivative having strong herbicidal action against weeds, particularly against weeds in paddy field which have not been easily controlled.

Another object of the present invention is to provide a process for preparing the above-mentioned novel pyrazole derivatives.

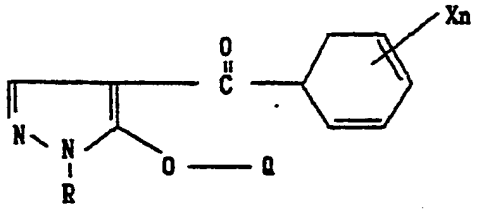
Further object of the present invention is to provide a selective herbicidal composition containing one or more of such pyrazole derivative(s) as an active ingredient.

Still further object of the present invention is to provide a novel pyrazole derivative which can control weeds in the field of corn. Among the compounds of the present invention, there are compounds which are very high as to safety to corn (Zea mays) and have also very strong activity against various kinds of weeds such as grass weeds, Cyperus esculeutus, yellow nutsedge, broadleaf-weeds, etc. in the field of corn; especially these compounds show high effects in controlling grass weeds at the vegetation period, which provide controlling technology which has not been accomplished by the conventional chemicals.

Other objects and features of the present invention will be apparent from the description hereinbelow.

DETAILED DESCRIPTION OF THE INVENTION

Pyrazole derivatives of the present invention are represented by the formula I:



(I)

wherein

R represents an alkyl group having 2 to 4 carbon atoms or an alkenyl group having 2 to 4 carbon atoms which may be substituted by halogen atom,

X represents a halogen atom, a lower alkyl group, nitro group, cyano group, a lower alkylsulfonyl group or trifluoromethyl group,

n represents an integer of 2 to 4,

Q represents hydrogen atom; an aralkyl group which may be substituted by halogen atom, nitro group, cyano group or a lower alkyl group; benzenesulfonyl group which may be substituted by a lower alkyl group or halogen atom; benzoyl group which may be substituted by a lower alkyl group or halogen atom; phenacyl group which may be substituted by a lower alkyl group or halogen atom; a lower alkyl group which may be substituted by halogen atom; a lower alkenyl group which may be substituted by halogen atom; or a lower alkynyl group.

Preferable substituents R are ethyl group, isopropyl group or allyl group; and most preferable ones are ethyl group or isopropyl group.

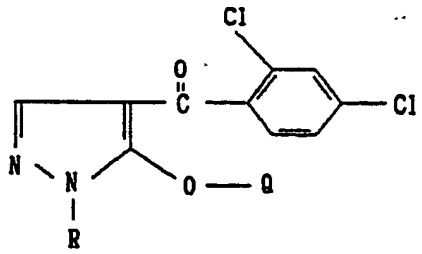
Preferable substituents X at 2-and 4-positions are halogen atom, lower alkyl group, nitro group, lower alkylsulfonyl group and trifluoromethyl group; and in case that they are unsubstituted, activity is generally lowered. Preferable substituents X at 3-position are lower alkyl group and halogen group, but this position may be unsubstituted. The most preferable substituents X are halogen atom including chlorine atom or methyl group, in 2-position; non-substitution or methyl group, at 3-position; and halogen atom including chlorine atom and methanesulfonyl group, in 4-position.

In case that Q represents except for hydrogen atom, Q is synthesized from a compound of hydrogen atom, which shows an actvity having basically the same property with compounds in which Q is hydrogen by various substituents. However, by introducing substituents into Q, there may often cause such cases that strongness or weakness of acitivity and weeding spectrum change; especially there may be a case that phytotoxicity to economic plants are further lowered. The above-mentioned substituents are selected from various kinds of substituents. In light of herbicidal activity, safety to the economic plants and ready production of compounds, the most preferable substituents are hydrogen atom, benzyl group, p-toluensulfonyl group, phenacyl group, methanesulfonyl group, acetyl group.

Preferred compounds of the formula I are those wherein R represents an alkyl group having 2 to 4 carbon atoms or allyl group, X represents a halogen atom, a lower alkyl group, nitro group, a lower alkylsulfonyl group or trifluoromethyl group, n is an integer 2 to 4, and Q represents benzyl, tosyl, methanesulfonyl, benzoyl, phenacyl, allyl, propargyl group or hydrogen atom.

Another preferred compounds of the formula I are those wherein R represents ethyl or isopropyl group, X represents a halogen atom, a lower alkyl group or methanesulfonyl group, n is an integer 2 to 4, and Q represents hydrogen atom, benzyl, tosyl, mesyl, phenacyl, allyl or propargyl group.

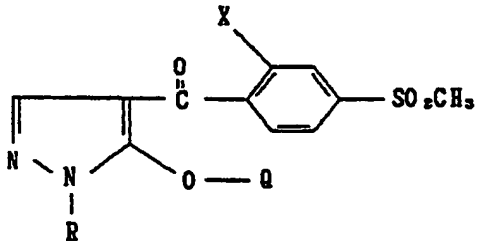
More preferred compounds are those of the formula V:



(V)

wherein R represents ethyl or isopropyl group, and Q represents hydrogen atom, benzyl or phenacyl group.

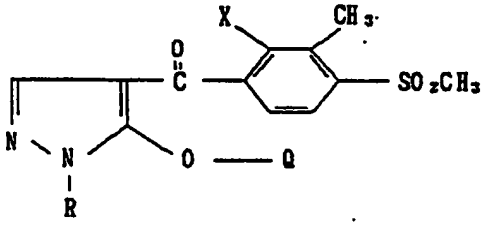
Particularly preferred compounds are those of the formula VI:



(VI)

wherein R represents ethyl or isopropyl group, X represents methyl group or chlorine atom and Q represents hydrogen atom or benzyl group.

More especially preferred compounds are those of the formula VII:



(VII)

(b)

wherein R represents ethyl or isopropyl group, X represents methyl group or chlorine atom and Q represents hydrogen atom or benzyl group.

Compounds having the best combinations of R, X and Q are:

4-(2,4-dichlorobenzoyl)-1-ethyl-5-benzyloxypyrazole,

4-(2,4-dichlorobenzoyl)-1-isopropyl-5-benzyloxypyrazole,

4-(2-chloro-4-methanesulf nylbenzoyl)-1-ethyl-5-hydroxypyrazole

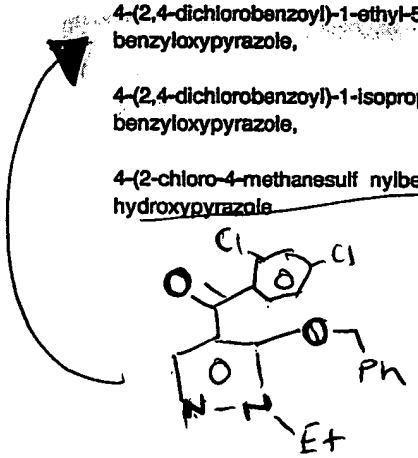
4-(2-chloro-3-methyl-4-methanesulfonylbenzoyl)-1-ethyl-5-hydroxypyrazole

4-(2-chloro-4-methanesulfonylbenzoyl)-1-isopropyl-5-hydroxylpyrazole

4-(2-chloro-3-methyl-4-methanesulfonylbenzoyl)-1-isopropyl-5-hydroxypyrazole

4-(2-methyl-4-methanesulfonylbenzoyl)-1-ethyl-5-hydroxypyrazole

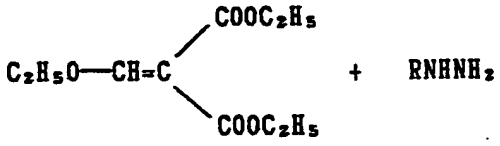
4-(2-m thyl-4-methanesulfonylbenzoyl)-1-isopropyl-5-hydroxypyrazole

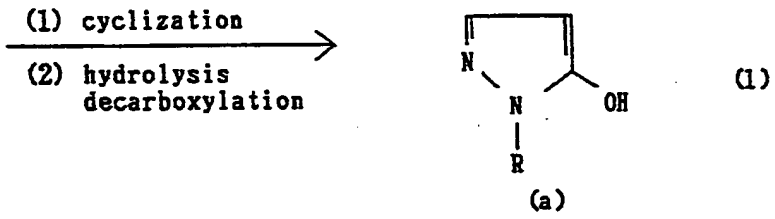


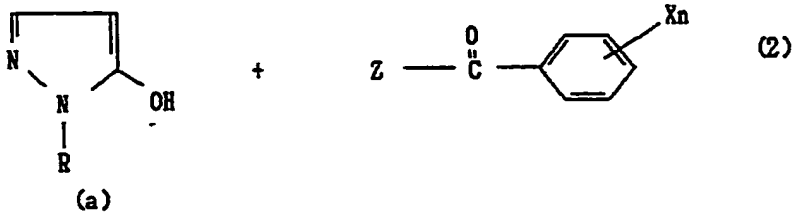
4-(2,3-dimethyl-4-methan sulfonylbenzoyl)-1-ethyl-5-hydroxypyrazole

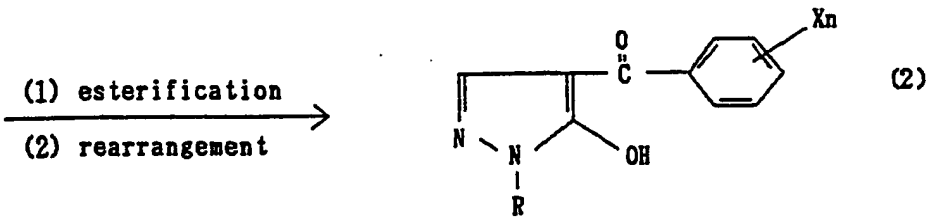
4-(2,3-dimethyl-4-methanesulfonylbenzoyl)-1-isopropyl-5-hydroxypyrazole

The compounds of the formula I may be readily prepared according to the following reaction - scheme:



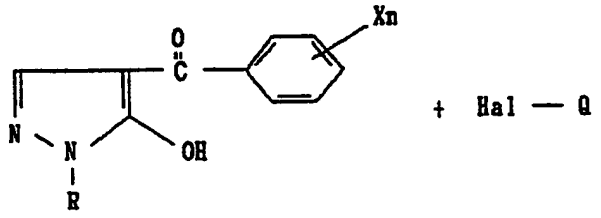




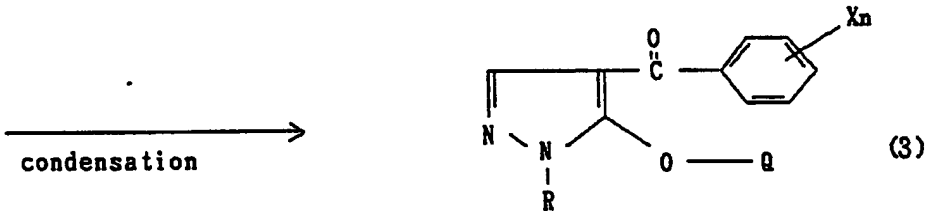


(2)

(b)



(b)



(3)

(I)

wherein

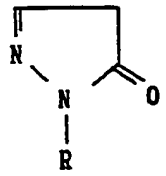
Z represents a halogen atom or hydroxyl group, preferably chlorine,

Hal represents a halogen atom, preferably chlorine or bromine, and R, X, Q and n each have the same meanings as defined in formula I.

Reaction (1) represents a reaction series comprising (i) synthesizing 4-carboethoxy-5-hydroxy-1-alkyl(alkenyl)pyrazole from a diethyl ethoxymethylene malonate and alkyl(alkenyl)hydrazine through cyclization reaction, followed by (ii) hydrolizing with mineral acid such as hydrochloric acid, etc. and decarboxylating the resulting compound to obtain 5-hydroxy-1-alkyl(alkenyl)-pyrazole. The cyclization reaction is performed at a temperature from -50 °C to 200 °C, preferably from -20 °C to 100 °C in an inert solvent such as methanol, ethanol, water, dioxane, benzene or toluene.

The hydrolysis and decarboxylation is performed at a temperature from 50 °C to 150 °C, preferably around boiling point of the solvent used in cyclization reaction. All of compounds (a) which are an intermediate of the present inv ntion are novel substances and group of compounds which

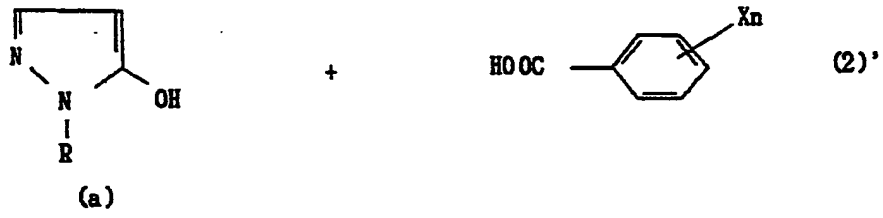
can be utilized as an intermediate for medicine and agricultural chemicals. In this connection, the compound (a) is a tautomer with the same compound with a compound (a') shown by the following formula (a'):



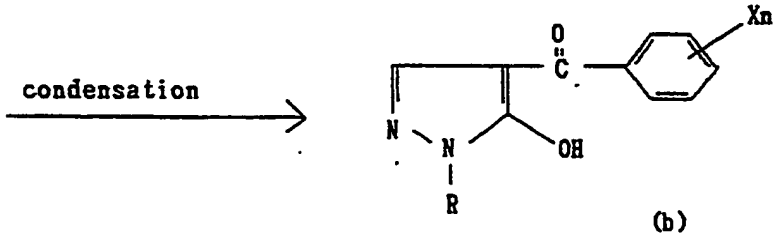
(a')

The compounds (b) can be prepared from compound (a) as a starting material through, for example, Reaction (2). For example, compounds (b) may be prepared by reacting compound (a) with a substituted benzoyl halide in an inert solvent in the presence of a dehydrohalogenating agent, preferably such as sodium hydroxide, potassium hydroxide, sodium carbonate or triethylamine to produce the corresponding esters and then effecting rearrangement of the esters to obtain the compounds (b). As the solvent for the esterification reaction may be used, for example, organic solvents such as dioxane, acetonitrile, benzene, toluene or chloroform alone or in combination with each other or with water, namely two phase systems such as water-toluene, water-chloroform and the like. Preferred solvents, however, for the esterification are water-chloroform two phase system. The rearrangement of the ester is performed by heating the ester with potassium carbonate or sodium carbonate in an inert solvent such as doxane at a temperature from 50°C to 150 °C

Instead of Reaction (2), the compound (b) may readily be synthesized by Reaction (2)':



(a) (2)'



(b)

performed by heating the ester with potassium carbonate or sodium carbonate in an inert solvent such as doxane at a temperature from 50°C to 150 °C

Instead of Reaction (2), the compound (b) may readily be synthesized by Reaction (2)':

According to this reaction, the objective compound (b) can be obtained readily and in a good yield in one step by reacting the compound (a) with appropriate substituted benzoic acid under the presence of an appropriate condensing agent and a basic substance.

As a dehydrating condensing agent used in this reaction, carbodimides such as N,N'-dicyclohexyl carbodiimide, N,N'-diisopropyl carbodiimide, N,N'-diethyl carbodiimide, N-cyclohexyl-N'-morpholinoethyl carbodiimide are suitable.

Suitable basic substances are, for example, sodium carbonate, potassium carbonate, sodium methoxide, potassium ethoxide and potassium-tertiary-butoxide.

Furthermore, this reaction is carried out in an inert solvent. For example, it is desirable to use alcohols such as isopropanol, tert.-butanol, sec-butanol, tert.-amylalcohol, but Ketones such as methyethyl ketone, diethyl ketone, etc. and nitriles such as acetonitrile, propionitrile, etc. may be used.

The reaction is completed between 30 minutes and 10 hours by mixing the compound (a), substituted benzoic acid, dehydrating condesning agent having eqaul mole, a basic substance having a half to equal mole in the solvent and heating the mixture. The reaction temperature is not especially limited, but is desirable to determine the temperature between 50 °C and a boiling point of a solvent to be used.

After the reaction, the objective compound (b) is obtained in the form of metal salt. Moreover, the compound (b) which is the free form can be readily isolated by using appropriate acid to adjust pH to <3.

Reaction (3) represents a condensation reaction of an in termediate (b) with an appropriate halide such as benzyl chloride, tosyl chloride to produce the compound of the formula I. This reaction is preferably carried out in a solvent which is inert to the reaction in the presence of a dehydrohalogenating agent. Suit able inert solvents are, for example, ethers such as diethyl ether, tetrahydrofuran and dioxane, aromatic hydrocarbons such as benzene, toluene and xylene, ketones such as acetone, methylethyl-ketone, halogenated hydrocarbons such as dichloromethane, chloroform and carbon tetrachloride, ethyl acetate, N,N-dimethylformamide, acetonitrile and the mixtures thereof. Among these solvents preferred ones are benzene, toluene, acetone and acetonitrile. Suitable dehydrohalogenating agents for Reaction - (3) are, for example, inorganic bases such as sodium carbonate, and potassium carbonate, and organic bases such as pyridine, triethylamine and N,N-diethylaniline, and preferably triethylamine.

Th reaction temperature ranges from room temperature to the boiling point of the solvent employed. However, it is most advantageous to effect the reaction at the boiling point of the solvent from the viewpoint of operation. By selecting the above-mentioned reaction conditions of the condensation reaction (3) appropriately, the compounds of the formula (I) can be obtained in a quite high yield.

Synthesis of the compounds according to the present invention is illustrated by way of the following examples which do not restrict the present invention.

SYNTHESIS EXAMPLE 1: Synthesis of 1-ethyl-5-hydroxypyrazole

A solution of 10.8 g (0.05 mol) of ethoxymethylenemalonate diethyl ester in 20 ml of ethanol was cooled to 0 °C. To the solution was added dropwise 10 g (0.05 mol) of 30 % aqueous solution of ethylhydrazine, while keeping the reaction temperature at below 5 °C. After the completion of the dropwise addition, the resulting mixture was stirred for 1 hours at room temperature, and then refluxed for 3 hour. After the completion of the reaction, the solvent in the mixture was distilled off under reduced pressure and concentrated. Then, the residue was added with 20 ml of 35 % hydrochloric acid and was subjected to hydrolysis and decarbonating reaction at the reflux temperature for 3 hours. After the completion of the reaction, the solvent was distilled off under the reduced pressure and dried to obtain 5.3 g of 1-ethyl-5-hydroxy-pyrazole as its hydrochloride. Yield: 72 %

^{1}H-NHR (δ, ppm, $CDCl_3$-DMSO-d_6):

1,42 (3H, t, J=7Hz, C $\underline{H_3}$), 4.20 (2H, q, J=7Hz, $C\underline{H_2}$-CH_3), 5.91 (1H, d, J=3Hz, pyrazole), 7.84 (1H, d, J=3Hz, pyrazole), 12.4 (2H, braod s)

SYNTHESIS EXAMPLE 2: Synthesis of 4-(2,4-dichlorobenzoyl)-1-ethyl-5-hydroxypyrazole

To an aqueous solution of 13.2 g (0.2 mol)of potassium hydroxide (pure degree: 85 %) dissolved in 55 ml of water was portionwise added 14.85 g (0.1 mol) of 1-ethyl-5-hydroxy-pyrazole hydrochloride with stirring under the ice cooling and neutralized to obtain its potassium salt. Thereafter, 60 ml of chloroform was added to the reaction mixture to prepare two layers. In the resulting mixture was dropwise added 20.95 g (0.1 mol) of 2,4-dichlorobenzoyl chloride while keeping the temperature at below 5°C and the mixture was stirred at room temperature for 2 hours, followed by addi-

ti n stirring for 1 hour at 40°C, and then, the reaction was ceased. After cooling the reaction solution, the organic layer was separated, washed successively with 5 % aqueous sodium bicarbonate, water and saturated brine and, after drying over sodium sulfate anhydride, the solvent was distilled off under reduced pressure and the remaining mixture was dried and caked to give a crude product of 5-(2,4-dichlorobenzoyloxy)-1-ethylpyrazole. Then, thus obtained ester-form crude product was added with 10 ml of 1,4-dioxane and dissolved, and was added with 20.7 g (0.15 mol) of anhydrous potassium carbonate at 120 °C. The resulting mixture was continued to heat with stirring for about 1 hour to solidify the reaction mixture. The obtained solid product was added with 50 ml of water and heated to be dissolved. After the dissolution, the temperature was cooled to the room temperature, and the dissolved mixture was added with hydrochloric acid to be adjusted to pH <1. The precipitated solid product which was obtained by filtration was dried and and recrystalliezed from a mixture of n-hexane-benzene to obtain 22.5 g of 4-(2,4-dichlorobenzoyl)-1-ethyl-5-hydroxypyrazole.

Yield: 79 %

m.p.: 144 -146 °C

^{1}H-NMR (δ, ppm, $CDCl_3$): 1.43 (3H, t, J=7Hz, -$\underline{CH_3}$), 4.04 (2H, q, J=7Hz, -$\underline{CH_2}$-), 7.30 -7.47 (4H, m), 9.57 (1H, S, -OH)

SYNTHESIS EXAMPLE 3: Synthesis of 4-(2,4-dichlorobenzoyl)-1-ethyl-5-benzyloxypyrazole

To 30 ml of benzene was added 1.43 g (0.005 mol) of 4-(2,4-dichlorobenzoyl)-1-ethyl-5-hydroxypyrazole and additionally added 0.51 g (0.005 mol) of triethylamine to prepare homogeneous solution.

To the solution was added 0.86 g (0.005 mol) of benzyl bromide with stirring at the room temperature and then, heated and reacted at the reflux temperature for 4 hours. After the reaction mixture thus obtained was cooled, the prepared salt was filtered off. The obtained benzene solution was washed successively with 5 % aqueous solution of sodium bicarbonate, water and saturated brine, and dried with anhydrous sodium sulfate. Then, the benzene was distilled off under reduced pressure to give oily residue. The resulting oil was purified through a silica gel column chromatography - (eluent:benzene) to obtain 1.41 g of the objective 4-(2,4-dichlorobenzoyl)-1-ethyl-5-benzyloxypyrazole as colorless oily product.

Yield: 75 %

^{1}H-NMR (δ, ppm, $CDCl_3$): 1.19 (3H, t, J=7Hz, -$\underline{CH_3}$), 3.83 (2H, t, J=7Hz, -$\underline{CH_2}CH_3$), 5.48 (2H, s, -$\underline{CH_2}$O-), 7.20 -7.40 (m, 9H)

SYNTHESIS EXAMPLE 4: Synthesis of 1-ethyl-4-(2-chloro-4-methanesulfonylbenzoyl)-5-hydroxyprazole

After 2.35 g (0.021 mol) of 1-ethyl-5-hydroxypyrazole was dissolved in 20 ml of tert.-amyl alcohole, the mixture was succesively added with 4.69 g (0.02 mol) of 2-chloro-4-methanesulfonyl benzoic acid, 5.33 g (0.021 mol) of N,N'-dicyclohexyl carbodiimide and 1.52 g (0.011 mol) of anhydrous potassium carbonate, and heated at 50 -60 °C for 5 hours, followed by additional stirring for 1 hour at 90 °C. Then, the reaction was ceased. After cooling, solvent was distilled off from the reaction solution, and the residue was added with 50 ml of 5% aqueous solution of potassium hydrox ide to dissolve the soluble matter. After insoluble matter was filtered off, the aqueous layer was washed with chloroform and separated. This operation was twice carried out. The obtained aqueous layer was adjusted to pH < 1 by adding concentrated hydrochloric acid, and the precipitated solid product was dissolved in chloroform and extracted. After the chloroform layer was dried over sodium sulfate anhydrate, the solvent was distilled off to give a crude product of the objective product. Then, the crude product was recrystallized from 95 % ethanol to obtain 5.38 g of 1-ethyl-4-(2-chloro-4-methanesulfonylbenzoyl)-5-hydroxypyrazole.

Yield: 82 %

m.p.: 172.0 -175.0 °C

SYNTHESIS EXMAPLLE 5: Synthesis of 1-ethyl-4-(2-chloro-3-methyl-4-methanesulfonylbenzoyl)-5-hydroxypyrazole

5.34 g of the objective 1-ethyl-4-(2-chloro-3-methyl-4-methanesulfonylbenzoyl)-5-hydroxypyrazole were obtained in the same operation and treatment as the Synthesis Examples 4 except that 4.69 g (0.02 mol) of 2-chloro-4-methanesulfonyl benzoic acid were replaced by

4.97 g (0.02 mol) of 2-chl ro-3-methyl-4-methanesulfonyl benzoic acid.

Yield: 78 %

m.p.: 225.0 -227.0 °C

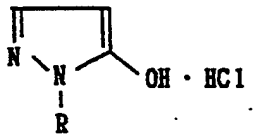
SYNTHESIS EXAMPLE 6: Synthesis of 4-(2-chloro-4-methane sulfonyl)-1-ethyl-5-hydroxypyrazole

1.5 g (0.01 mol) of 1-ethyl-5-hydroxypyrazole hydrochloride was portionwise added to a solution of 1.3 g of potassium hydroxide (purity: 85 %) in 10 ml of water with stirring under ice-cooling to give potassium salt thereof. Then, 10 ml of chloroform was added to the mixture to form two layers. To the two-layer mixture was portionwise added 2.5 g (0.01 mol) of 2-chloro-4-methanesulfonylbenzoyl chloride by keeping the temperature at below 5 °C. The resulting mixture was stirred at the room temperature for 2 hours, followed by further stirring at 40°C for 1 hour. After the reaction mixture was cooled, the chloroform layer was separated, and was succesively washed with 5% aqueous solution of $NaHCO_3$, water, saturated brine. Then, the reaction mixture was dried over sodium sulfate anhydride and the solvent was distilled off under reduced pressure. The residue was dissolved in 2 ml of 1,4-dioxane and heated to 120°C and then, was added with 2.1 g (0.015 mol) of anhydrous potassium carbonate at 120°C and further heated for about 3 hours. After the temperature was left to cool to 90 °C, the mixture was added water and dissolved, then the temperature was returned to the room temperature. After that, the mixture was adjusted to pH < 1 by adding hydrochlo ric acid. The precipitated solid matter was filtered, dried and recrystallized from ethanol to obtain 1.8 g of the title compound.

Yield: 55 %

The compounds listed in Table 1 were synthesized in the same manner as Synthesis Example 1. However, the present invention was not limited to these compounds.

Table 1



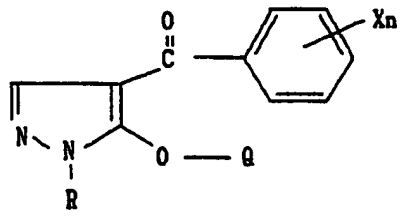
R	Yield (%)	^{1}H-NMR(δ, ppm) [solvent]
C_2H_5	72	1.42 (3H, t, J=7Hz, CH_3), 4.20 (2H, q, J=7Hz, -$\underline{CH_2}$ -CH_3), 5.91 (1H, d, J=3Hz, =CH-), 7.84(1H, d, J=3Hz, =CH-), 12.4 (2H, broad s) [$CDCl_3$-DMSO-d_6]
C_3H_7	66	0.91(3H, t, J=7Hz, CH_3), 1.90 (2H, t, q, J=7Hz, -CH_2 $\underline{CH_2}$ CH_3), 4.14 (2H, t, J=7Hz, $\underline{CH_2}$ CH_2 CH_3), 5.92 (1H, d, J=3Hz, =CH-), 7.73 (1H,= CH-), 11.0 (2H, broad s) [$CDCl_3$-DMSO-d_6]
$CH(CH_3)_2$	68	1.56 (6H, d, J=7Hz, -$CH(\underline{CH_3})_2$), 4.82(1H, q, q, J=7Hz, -$\underline{CH}(CH_3)_2$), 5.97 (1H, d, J=3.5Hz, =CH-), 7.90 (1H, d, J=3.5Hz,=CH-), 10.68 (2H, broad s) [$CDCl_3$-DMSO-d_6]

Table 1 (cont'd)

$CH_2C(Cl)=CH_2$	53	4.98(2H, s, =N-CH_2 -), 5.43(1H,d, J=2Hz, =C=CH_2), 5.60(1H, d, J=2Hz =C=CH_2), 5.94(1H, d, J=3Hz, =CH-), 7.73 (1H, d, J=3Hz, =CH-) ($CDCl_3$ + DMSO-d_6)
$CH_2CH=CH_2$	61	4.80(2H, d, J=5Hz, =N-CH_2-), 5.06 ~6.20 (3H, m, -CH=CH_2), 5.97(1H, d, J=3Hz, =CH-), 7.85(1H, d, J= 3Hz, =CH-) ($CDCl_3$+DMSO-d_6)
$C(CH_3)_3$	46	1.68(9H, s, $C(CH_3)_3$), 6.08(1H, d, J=3.5 Hz, =CH-), 7.79(1H, d, J= 3.5Hz, =CH-), 10.65 (2H, s) ($CDCl_3$ -DMSO-d_6)

The compounds synthesized according to Synthesis Examples 2 -5 are listed in Table 2.

Table 2



Compound No.	R	Xn	Q	m.p.(℃)
1	Et	2,4-Cl_2	H	144 - 146
2	Et	2,4-Cl_2	benzyl	oil (NMR-2)
3	Et	2,4-Cl_2	tosyl	oil (NMR-3)
4	Et	2,4-Cl_2	phenacyl	97.5 - 99
5	Et	2,4-Cl_2	mesyl	
6	Et	2,4-Cl_2	acetyl	
7	Et	2,4-Cl_2	α-methyl-benzyl	oil (NMR-7)
8	Et	2,4-Cl_2	2-chloro-benzyl	oil (NMR-8)
9	Et	2,4-Cl_2	4-nitro-benzyl	100 - 102
10	Et	2,4-Cl_2	2-methyl-benzyl	oil (NMR-10)
11	Et	2,4-Cl_2	2-chloro-allyl	oil (NMR-11)
12	Et	2,4-Cl_2	propar-gyl	oil (NMR-12)
13	Et	2,4-Cl_2	2,4-dichlo-robenzoyl	174.5 - 175
14	Et	2,4-Cl_2	benzoyl	
15	Et	2,4-Cl_2	4-methyl-phenacyl	
16	Et	2,4-Cl_2	α-methyl-phenacyl	
17	Et	2,4-Cl_2	2,4-dichlo-benzyl	

Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p.(℃)
18	Et.	2-Cl-4-SO_2CH_3	H	172 - 175
19	Et.	2-Cl-4-SO_2CH_3	benzyl	126 - 129
20	Et.	2-Cl-4-SO_2CH_3	tosyl	150 - 151
21	Et.	2-Cl-4-SO_2CH_3	phenacyl	172 - 173
22	Et.	2-Cl-4-SO_2CH_3	mesyl	204 - 206
23	Et.	2-Cl-4-SO_2CH_3	acetyl	
24	Et.	2-Cl-4-SO_2CH_3	benzoyl	
25	Et.	2-Cl-4-SO_2CH_3	α-methyl-benzyl	
26	Et.	2-Cl-4-SO_2CH_3	2-methyl-benzyl	
27	Et.	2-Cl-4-SO_2CH_3	2-chloro-benzyl	
28	Et.	2-Cl-3-CH_3-4-SO_2CH_3	H	225 - 227
29	Et.	2-Cl-3-CH_3-4-SO_2CH_3	benzyl	oil(NMR-29)
30	Et.	2-Cl-3-CH_3-4-SO_2CH_3	tosyl	
31	Et.	2-Cl-3-CH_3-4-SO_2CH_3	phenacyl	
32	Et.	2-Cl-3-CH_3-4-SO_2CH_3	mesyl	
33	Et.	2-Cl-3-CH_3-4-SO_2CH_3	acetyl	
34	Et.	2-Cl-3-CH_3-4-SO_2CH_3	benzoyl	
35	Et.	2-Cl-3-CH_3-4-SO_2CH_3	α-methyl-benzyl	
36	Et.	2-Cl-3-CH_3-4-SO_2CH_3	2-methyl-benzyl	

Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p.(℃)
37	Et.	2-Cl-3-CH_3-4-SO_2CH_3	2-chloro-benzyl	
38	Et.	2,4-Cl_2-3-CH_3	H	126 -127
39	Et.	2,4-Cl_2-3-CH_3	benzyl	oil(NMR-39)
40	Et.	2,4-Cl_2-3-CH_3	tosyl	
41	Et.	2,4-Cl_2-3-CH_3	phenacyl	oil(NMR-41)
42	Et.	2,4-Cl_2-3-CH_3	2-chloro-benzyl	oil(NMR-42)
43	Et.	2-NO_2-4-Cl	H	174 - 176
44	Et.	2-NO_2-4-Cl	benzyl	oil(NMR-44)
45	Et.	2-NO_2-4-Cl	tosyl	oil(NMR-45)
46	Et.	2-NO_2-4-Cl	phenacyl	
47	Et.	2-Cl-4-SO_2CH_3	allyl	
48	Et.	2-Cl-4-SO_2CH_3	propargyl	
49	Et.	2-Cl-3-CH_3-4-SO_2CH_3	allyl	
50	Et.	2-Cl-3-CH_3-4-SO_2CH_3	propargyl	
51	Et.	2-Cl-4-SO_2CH_3	methyl	
52	Et.	2-Cl-3-CH_3-4-SO_2CH_3	methyl	
53	Et.	2-Br-4-SO_2CH_3	H	157 - 163
54	Et.	2-Br-4-SO_2CH_3	benzyl	
55	Et.	2-Br-4-SO_2CH_3	tosyl	
56	Et.	2-Br-4-SO_2CH_3	phenacyl	
57	Et.	2-Br-4-SO_2CH_3	mesyl	

Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p.(℃)
58	Et.	2-Br-4-SO_2CH_3	acetyl	
59	Et.	2-Br-3-CH_3-4-SO_2CH_3	H	
60	Et.	2-Br-3-CH_3-4-SO_2CH_3	benzyl	
61	Et.	2-Br-3-CH_3-4-SO_2CH_3	tosyl	
62	Et.	2-Br-3-CH_3-4-SO_2CH_3	phenacyl	
63	Et.	2-Br-3-CH_3-4-SO_2CH_3	mesyl	
64	Et.	2-Br-3-CH_3-4-SO_2CH_3	acetyl	
65	Et.	2-F-4-SO_2CH_3	H	
66	Et.	2-F-4-SO_2CH_3	benbyl	
67	Et.	2-F-4-SO_2CH_3	tosyl	
68	Et.	2-F-4-SO_2CH_3	phenacy	
69	Et.	2-F-4-SO_2CH_3	mesyl	
70	Et.	2-F-4-SO_2CH_3	acetyl	
71	Et.	2-F-3-CH_3-4-SO_2CH_3	H	
72	Et.	2-F-3-CH_3-4-SO_2CH_3	benzyl	
73	Et.	2-F-3-CH_3-4-SO_2CH_3	tosyl	
74	Et.	2-CH_3-4-SO_2CH_3	H	160 - 164
75	Et.	2-CH_3-4-SO_2CH_3	benzyl	
76	Et.	2-CH_3-4-SO_2CH_3	tosyl	
77	Et.	2-CH_3-4-SO_2CH_3	phenacyl	154 - 157
78	Et.	2-CH_3-4-SO_2CH_3	mesyl	
79	Et.	2-CH_3-4-SO_2CH_3	acetyl	

Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p.(℃)
80	Et.	2,3-$(CH_3)_2$-4-SO_2CH_3	H	202 - 203
81	Et.	2,3-$(CH_3)_2$-4-SO_2CH_3	tosyl	
82	Et.	2,3-$(CH_3)_2$-4-SO_2CH_3	phenacyl	
83	Et.	2,3-$(CH_3)_2$-4-SO_2CH_3	mesyl	
84	Et.	2,3-$(CH_3)_2$-4-SO_2CH_3	acetyl	
85	Et.	2,3-$(CH_3)_2$-4-SO_2CH_3	benzyl	oil(NMR-85)
86	Et.	2,3-Cl_2-4-SO_2CH_3	H	
87	Et.	2,3-Cl_2-4-SO_2CH_3	benzyl	
88	Et.	2,3-Cl_2-4-SO_2CH_3	phenacyl	
89	Et.	2,3-Cl_2-4-SO_2CH_3	tosyl	
90	Et.	2,3-Cl_2-4-SO_2CH_3	mesyl	
91	Et.	2,3-Cl_2-4-SO_2CH_3	acetyl	
92	Et.	2-Cl-3-Et-4-SO_2CH_3	H	
93	Et.	2-Cl-3-Et-4-SO_2CH_3	benzyl	
94	Et.	2-Cl-3-Et-4-SO_2CH_3	phenacyl	
95	Et.	2-Cl-3-Et-4-SO_2CH_3	tosyl	
96	Et.	2-Cl-3-Et-4-SO_2CH_3	mesyl	
97	Et.	2-Cl-3-Et-4-SO_2CH_3	acetyl	
98	Et.	2,4-$(SO_2CH_3)_2$	H	
99	Et.	2,4-$(SO_2CH_3)_2$	benzyl	
100	Et.	2,4-$(SO_2CH_3)_2$	tosyl	
101	Et.	2,4-$(SO_2CH_3)_2$	mesyl	

Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p.(℃)
102	Et.	2,4-$(SO_2CH_3)_2$	acetyl	
103	Et.	2,4-$(SO_2CH_3)_2$	phenacyl	
104	Et.	2,4-$(SO_2CH_3)_2$-3-CH_3	H	
105	Et.	2,4-$(SO_2CH_3)_2$-3-CH_3	benzyl	
106	Et.	2,4-$(SO_2CH_3)_2$-3-CH_3	tosyl	
107	Et.	2,4-$(SO_2CH_3)_2$-3-CH_3	phenacyl	
108	Et.	2,4-$(SO_2CH_3)_2$-3-CH_3	mesyl	
109	Et.	2,4-$(SO_2CH_3)_2$-3-CH_3	acetyl	
110	Et.	2-CN-4-SO_2CH_3	H	

Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p. (℃)
111	Et.	2-CN-4-SO_2CH_3	benzyl	
112	Et.	2-CN-4-SO_2CH_3	tosyl	
113	Et.	2-CN-4-SO_2CH_3	phenacyl	
114	Et.	2-CN-4-SO_2CH_3	mesyl	
115	Et.	2-CN-4-SO_2CH_3	acetyl	
116	Et.	2-CN-3-CH_3-4-SO_2CH_3	H	
117	Et.	2-CN-3-CH_3-4-SO_2CH_3	benzyl	
118	Et.	2-CN-3-CH_3-4-SO_2CH_3	tosyl	
119	Et.	2-I-4-SO_2CH_3	H	
120	Et.	2-I-4-SO_2CH_3	benzyl	
121	Et.	2-I-4-SO_2CH_3	tosyl	
122	Et.	2-I-3-CH_3-4-SO_2CH_3	H	
123	Et.	2-I-3-CH_3-4-SO_2CH_3	benzyl	
124	Et.	2-Cl-4-SO_2Et	H	
125	Et.	2-Cl-4-SO_2Et	benzyl	
126	Et.	2-Cl-4-SO_2Et	tosyl	
127	Et.	2-Cl-4-SO_2 ^{i} P $_{r}$	H	156 - 158
128	Et.	2-Cl-4-SO_2 ^{i} P $_{r}$	benzyl	104 - 105.5
129	Et.	2-Cl-4-SO_2 ^{i} P $_{r}$	tosyl	
130	Et.	2-Cl-4-SO_2 ^{n} P $_{r}$	H	153 - 154
131	Et.	2-Cl-4-SO_2 ^{n} P $_{r}$	benzyl	oil(NMR-131)

Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p. (℃)
132	Et.	2-Cl-4-SO_2 ^{n} P $_r$	tosyl	115 - 116
133	Et.	2-NO_2-4-SO_2CH_3	H	
134	Et.	2-NO_2-4-SO_2CH_3	benzyl	
135	Et.	2-NO_2-4-SO_2CH_3	tosyl	
136	Et.	2-NO_2-4-SO_2CH_3	mesyl	
137	Et.	2-NO_2-4-SO_2CH_3	phenacyl	
138	Et.	2-NO_2-4-SO_2CH_3	acetyl	
139	Et.	2-SO_2CH_3-5-CH_3	H	
140	Et.	2-SO_2CH_3-5-CH_3	benzyl	
141	Et.	2-SO_2CH_3-5-CH_3	tosyl	
142	Et.	2-NO_2-3-CH_3-4-SO_2CH_3	H	
143	Et.	2-NO_2-3-CH_3-4-SO_2CH_3	benzyl	
144	Et.	2-NO_2-3-CH_3-4-SO_2CH_3	tosyl	
145	^{i} P $_r$	2,4-Cl_2	H	151 - 154
146	^{i} P $_r$	2,4-Cl_2	benzyl	oil(NMR-146)
147	^{i} P $_r$	2,4-Cl_2	phenacyl	
148	^{i} P $_r$	2,4-Cl_2	tosyl	
149	^{i} P $_r$	2,4-Cl_2	α-methyl benzyl	
150	^{i} P $_r$	2,4-Cl_2	2-chloro benzyl	
151	^{i} P $_r$	2,4-Cl_2	2-methyl benzyl	
152	^{i} P $_r$	2-Cl-4-SO_2CH_3	H	181 - 184
153	^{i} P $_r$	2-Cl-4-SO_2CH_3	benzyl	164 - 166

65

Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p. (℃)
154	^{i}Pr	2-Cl-4-SO_2CH_3	phenacyl	
155	^{i}Pr	2-Cl-4-SO_2CH_3	tosyl	
156	^{i}Pr	2-Cl-4-SO_2CH_3	mesyl	
157	^{i}Pr	2-Cl-4-SO_2CH_3	benzoyl	
158	^{i}Pr	2-Cl-4-SO_2CH_3	acetyl	
159	^{i}Pr	2-Cl-4-SO_2CH_3	propargyl	
160	^{i}Pr	2-Cl-4-SO_2CH_3	allyl	
161	^{i}Pr	2-Cl-4-SO_2CH_3	methyl	
162	^{i}Pr	2-Cl-3-CH_3-4-SO_2CH_3	H	179 - 181.5
163	^{i}Pr	2-Cl-3-CH_3-4-SO_2CH_3	benzyl	
164	^{i}Pr	2-Cl-3-CH_3-4-SO_2CH_3	phenacyl	
165	^{i}Pr	2-Cl-3-CH_3-4-SO_2CH_3	tosyl	
166	^{i}Pr	2-Cl-3-CH_3-4-SO_2CH_3	mesyl	
167	^{i}Pr	2-Cl-3-CH_3-4-SO_2CH_3	benzoyl	
168	^{i}Pr	2-Cl-3-CH_3-4-SO_2CH_3	acetyl	
169	^{i}Pr	2-Cl-3-CH_3-4-SO_2CH_3	propargyl	
170	^{i}Pr	2-Cl-3-CH_3-4-SO_2CH_3	allyl	
171	^{i}Pr	2-Cl-3-CH_3-4-SO_2CH_3	methyl	
172	^{i}Pr	2,4-Cl_2-3-CH_3	H	
173	^{i}Pr	2,4-Cl_2-3-CH_3	benzyl	
174	^{i}Pr	2,4-Cl_2-3-CH_3	tosyl	
175	^{i}Pr	2,4-Cl_2-3-CH_3	phenacyl	

Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p. (℃)
176	^{i}Pr	2-NO_2-4-Cl	H	
177	^{i}Pr	2-NO_2-4-Cl	benzyl	
178	^{i}Pr	2-Br-4-SO_2CH_3	H	
179	^{i}Pr	2-Br-4-SO_2CH_3	benzyl	
180	^{i}Pr	2-Br-4-SO_2CH_3	tosyl	
181	^{i}Pr	2-Br-3-CH_3-4-SO_2CH_3	H	
182	^{i}Pr	2-Br-3-CH_3-4-SO_2CH_3	benzyl	
183	^{i}Pr	2-Br-3-CH_3-4-SO_2CH_3	tosyl	
184	^{i}Pr	2-F-4-SO_2CH_3	H	
185	^{i}Pr	2-F-4-SO_2CH_3	benzyl	
186	^{i}Pr	2-F-4-SO_2CH_3	tosyl	
187	^{i}Pr	2-F-3-CH_3-4-SO_2CH_3	H	
188	^{i}Pr	2-F-3-CH_3-4-SO_2CH_3	benzyl	
189	^{i}Pr	2-F-3-CH_3-4-SO_2CH_3	tosyl	
190	^{i}Pr	2-CH_3-4-SO_2CH_3	H	
191	^{i}Pr	2-CH_3-4-SO_2CH_3	benzyl	
192	^{i}Pr	2-CH_3-4-SO_2CH_3	tosyl	
193	^{i}Pr	2,3-$(CH_3)_2$-4-SO_2CH_3	H	163 - 165
194	^{i}Pr	2,3-$(CH_3)_2$-4-SO_2CH_3	benzyl	oil (NMR-194)
195	^{i}Pr	2,3-$(CH_3)_2$-4-SO_2CH_3	tosyl	
196	^{i}Pr	2,3-Cl_2-4-SO_2CH_3	H	
197	^{i}Pr	2,3-Cl_2-4-SO_2CH_3	benzyl	

Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p. (℃)
198	^{i}Pr	2,3-Cl_2-4-SO_2CH_3	tosyl	
199	^{i}Pr	2-Cl-3-Et-4-SO_2CH_3	H	
200	^{i}Pr	2-Cl-3-Et-4-SO_2CH_3	benzyl	
201	^{i}Pr	2-Cl-3-Et-4-SO_2CH_3	tosyl	
202	^{i}Pr	2-Cl-3-Et-4-SO_2CH_3	mesyl	
203	^{i}Pr	2-Cl-3-Et-4-SO_2CH_3	acetyl	
204	^{i}Pr	2,4-$(SO_2CH_3)_2$	H	
205	^{i}Pr	2,4-$(SO_2CH_3)_2$	benzyl	
206	^{i}Pr	2,4-$(SO_2CH_3)_2$	tosyl	
207	^{i}Pr	2,4-$(SO_2CH_3)_2$-3-CH_3	H	
208	^{i}Pr	2,4-$(SO_2CH_3)_2$-3-CH_3	benzyl	
209	^{i}Pr	2,4-$(SO_2CH_3)_2$-3-CH_3	tosyl	
210	^{i}Pr	2-CN-4-SO_2CH_3	H	
211	^{i}Pr	2-CN-4-SO_2CH_3	benzyl	
212	^{i}Pr	2-CN-4-SO_2CH_3	tosyl	
213	^{i}Pr	2-CN-3-CH_3-4-SO_2CH_3	H	
214	^{i}Pr	2-CN-3-CH_3-4-SO_2CH_3	benzyl	
215	^{i}Pr	2-CN-3-CH_3-4-SO_2CH_3	tosyl	
216	^{i}Pr	2-I-4-SO_2CH_3	H	
217	^{i}Pr	2-I-4-SO_2CH_3	benzyl	
218	^{i}Pr	2-Cl-4-SO_2Et	H	
219	^{i}Pr	2-Cl-4-SO_2Et	benzyl	

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Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p. (℃)
220	^{i}Pr	2-Cl-4-$SO_2{}^{i}Pr$	H	148 - 151
221	^{i}Pr	2-Cl-4-$SO_2{}^{i}Pr$	benzyl	oil(NMR-221)
222	^{i}Pr	2-Cl-4-$SO_2{}^{n}Pr$	H	
223	^{i}Pr	2-Cl-4-$SO_2{}^{n}Pr$	benzyl	
224	^{i}Pr	2-NO_2-4-SO_2CH_3	H	
225	^{i}Pr	2-NO_2-4-SO_2CH_3	benzyl	
226	^{i}Pr	2-NO_2-4-SO_2CH_3	tosyl	
227	^{i}Pr	2-NO_2-3-CH_3-4-SO_2CH_3	H	
228	^{i}Pr	2-NO_2-3-CH_3-4-SO_2CH_3	benzyl	
229	^{i}Pr	2-NO_2-3-CH_3-4-SO_2CH_3	tosyl	
230	^{i}Pr	2-SO_2CH_3-5-CH_3	H	
231	allyl	2,4-Cl_2	H	
232	allyl	2,4-Cl_2	benzyl	oil(NMR-232)
233	allyl	2,4-Cl_2	tosyl	
234	allyl	2,4-Cl_2	phenacyl	
235	allyl	2-Cl-4-SO_2CH_3	H	
236	allyl	2-Cl-4-SO_2CH_3	benzyl	
237	allyl	2-Cl-4-SO_2CH_3	tosyl	
238	allyl	2-Cl-3-CH_3-4-SO_2CH_3	H	
239	allyl	2-Cl-3-CH_3-4-SO_2CH_3	benzyl	
240	allyl	2-Cl-3-CH_3-4-SO_2CH_3	tosyl	
241	allyl	2,4-Cl_2-3-CH_3	H	

Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p. (℃)
242	allyl	2,4-Cl_2-3-CH_3	benzyl	
243	allyl	2-NO_2-4-Cl	H	
244	allyl	2-Br-4-SO_2CH_3	H	
245	allyl	2-Br-4-SO_2CH_3	benzyl	
246	allyl	2-Br-3-CH_3-4-SO_2CH_3	H	
247	allyl	2-Br-3-CH_3-4-SO_2CH_3	benzyl	
248	allyl	2-F-4-SO_2CH_3	H	
249	allyl	2-F-4-SO_2CH_3	benzyl	
250	allyl	2-F-3-CH_3-4-SO_2CH_3	H	
251	allyl	2-CH_3-4-SO_2CH_3	H	
252	allyl	2-CH_3-4-SO_2CH_3	benzyl	
253	allyl	2-Cl-3-Et-4-SO_2CH_3	H	
254	allyl	2-Cl-3-Et-4-SO_2CH_3	benzyl	
255	allyl	2,3-$(CH_3)_2$-4-SO_2CH_3	H	
256	allyl	2,3-Cl_2-4-SO_2CH_3	H	
257	allyl	2-CN-4-SO_2CH_3	H	
258	allyl	2-CN-3-CH_3-4-SO_2CH_3	H	
259	allyl	2-I-4-SO_2CH_3	H	
260	allyl	2-I-3-CH_3-4-SO_2CH_3	H	
261	allyl	2-Cl-4-SO_2Et	H	
262	allyl	2-Cl-4-$SO_2{}^iPr$	H	
263	allyl	2-Cl-4-$SO_2{}^nPr$	H	

Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p. (℃)
264	allyl	2-NO_2-4-SO_2CH_3	H	
265	allyl	2-NO_2-4-SO_2CH_3	benzyl	
266	allyl	2-NO_2-3-CH_3-4-SO_2CH_3	H	
266	allyl	2-NO_2-3-CH_3-4-SO_2CH_3	benzyl	
267	allyl	2-SO_2CH_3-5-CH_3	H	
268	^{n}Pr	2,4-Cl_2	H	oil(NMR-268)
269	^{n}Pr	2,4-Cl_2	benzyl	oil(NMR-269)
270	^{n}Pr	2-Cl-4-SO_2CH_3	H	
271	^{n}Pr	2-Cl-4-SO_2CH_3	benzyl	
272	^{n}Pr	2-Cl-3-CH_3-4-SO_2CH_3	H	
273	^{n}Pr	2-Cl-3-CH_3-4-SO_2CH_3	benzyl	
274	^{n}Pr	2,4-Cl_2-3-CH_3	H	
275	^{n}Pr	2,4-Cl_2-3-CH_3	benzyl	
276	^{n}Pr	2-NO_2-4-Cl	H	
277	^{n}Pr	2-Br-4-SO_2CH_3	H	
278	^{n}Pr	2-Br-3-CH_3-4-SO_2CH_3	H	
279	^{n}Pr	2-F-4-SO_2CH_3	H	
280	^{n}Pr	2-F-3-CH_3-4-SO_2CH_3	H	
281	^{n}Pr	2-CH_3-4-SO_2CH_3	H	
282	^{n}Pr	2-Cl-3-Et-4-SO_2CH_3	H	
283	^{n}Pr	2,3-$(CH_3)_2$-4-SO_2CH_3	H	
284	^{n}Pr	2,3-Cl_2-4-SO_2CH_3	H	

Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p. (℃)
285	$^{n}P_{r}$	2-CN-4-SO_2CH_3	H	
286	$^{n}P_{r}$	2-CN-3-CH_3-4-SO_2CH_3	H	
287	$^{n}P_{r}$	2-I-4-SO_2CH_3	H	
288	$^{n}P_{r}$	2-I-3-CH_3-4-SO_2CH_3	H	
289	$^{n}P_{r}$	2-Cl-4-SO_2Et	H	
290	$^{n}P_{r}$	2-Cl-4-$SO_2{}^{i}P_{r}$	H	
291	$^{n}P_{r}$	2-Cl-4-$SO_2{}^{n}P_{r}$	H	
292	$^{n}P_{r}$	2,4-Cl_2	4-ethyl benzyl	oil(NMR-292)
293	$^{n}P_{r}$	2-NO_2-4-SO_2CH_3	H	
294	$^{n}P_{r}$	2-NO_2-3-CH_3-4-SO_2CH_3	H	
295	$^{n}P_{r}$	2-SO_2CH_3-5-CH_3	H	
296	$^{n}B_{u}$	2,4-Cl_2	H	oil(NMR-296)
297	$^{n}B_{u}$	2,4-Cl_2	benzyl	oil(NMR-297)
298	$^{n}B_{u}$	2-Cl-4-SO_2CH_3	H	
299	$^{n}B_{u}$	2-Cl-4-SO_2CH_3	benzyl	
300	$^{n}B_{u}$	2-Cl-3-CH_3-4-SO_2CH_3	H	
301	$^{n}B_{u}$	2-Cl-3-CH_3-4-SO_2CH_3	benzyl	
302	$^{n}B_{u}$	2,4-Cl_2-3-CH_3	H	
303	$^{n}B_{u}$	2,4-Cl_2-3-CH_3	benzyl	
304	$^{n}B_{u}$	2-NO_2-4-Cl	H	
305	$^{n}B_{u}$	2-Br-4-SO_2CH_3	H	
306	$^{n}B_{u}$	2-Br-3-CH_3-4-SO_2CH_3	H	

Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p. (℃)
307	^{n}Bu	2-F-4-SO_2CH_3	H	
308	^{n}Bu	2-F-3-CH_3-4-SO_2CH_3	H	
309	^{n}Bu	2-CH_3-4-SO_2CH_3	H	
310	^{n}Bu	2-Cl-3-Et-4-SO_2CH_3	H	
311	^{n}Bu	2,3-$(CH_3)_2$-4-SO_2CH_3	H	
312	^{n}Bu	2,3-Cl_2-4-SO_2CH_3	H	
313	^{n}Bu	2-CN-4-SO_2CH_3	H	
314	^{n}Bu	2-CN-3-CH_3-4-SO_2CH_3	H	
315	^{n}Bu	2-I-4-SO_2CH_3	H	
316	^{n}Bu	2-I-3-CH_3-4-SO_2CH_3	H	
317	^{n}Bu	2-Cl-4-SO_2Et	H	
318	^{n}Bu	2-Cl-4-$SO_2{}^{i}$Pr	H	
319	^{n}Bu	2-Cl-4-$SO_2{}^{n}$Pr	H	
320	^{n}Bu	2,4-Cl_2	2-chloro-benzyl	oil(NMR-320)
321	^{n}Bu	2-NO_2-4-SO_2CH_3	H	
322	^{n}Bu	2-NO_2-3-CH_3-4-SO_2CH_3	H	
323	^{n}Bu	2-SO_2CH_3-5-CH_3	H	
324	^{i}Bu	2,4-Cl_2	H	
325	^{i}Bu	2,4-Cl_2	benzyl	
326	^{i}Bu	2-Cl-4-SO_2CH_3	H	
327	^{i}Bu	2-Cl-4-SO_2CH_3	benzyl	
328	^{i}Bu	2-Cl-3-CH_3-4-SO_2CH_3	H	

Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p. (℃)
329	^{i} B $_{u}$	2-Cl-3-CH_3-4-SO_2CH_3	benzyl	
330	^{i} B $_{u}$	2,4-Cl_2-3-CH_3	H	
331	^{i} B $_{u}$	2,4-Cl_2-3-CH_3	benzyl	
332	^{i} B $_{u}$	2-NO_2-4-Cl	H	
333	^{i} B $_{u}$	2-Br-4-SO_2CH_3	H	
334	^{i} B $_{u}$	2-Br-3-CH_3-4-SO_2CH_3	H	
335	^{i} B $_{u}$	2-F-4-SO_2CH_3	H	
336	^{i} B $_{u}$	2-F-3-CH_3-4-SO_2CH_3	H	
337	^{i} B $_{u}$	2-CH_3-4-SO_2CH_3	H	
338	^{i} B $_{u}$	2-Cl-3-Et-4-SO_2CH_3	H	
339	^{i} B $_{u}$	2,3-$(CH_3)_2$-4-SO_2CH_3	H	
340	^{i} B $_{u}$	2,3-Cl_2-4-SO_2CH_3	H	
341	^{i} B $_{u}$	2-CN-4-SO_2CH_3	H	
342	^{i} B $_{u}$	2-CN-3-CH_3-4-SO_2CH_3	H	
343	^{i} B $_{u}$	2-I-4-SO_2CH_3	H	
344	^{i} B $_{u}$	2-I-3-CH_3-4-SO_2CH_3	H	
345	^{i} B $_{u}$	2-Cl-4-SO_2Et	H	
346	^{i} B $_{u}$	2-Cl-4-SO_2^{i} P $_{r}$	H	
347	^{i} B $_{u}$	2-Cl-4-SO_2^{n} P $_{r}$	H	
348	^{i} B $_{u}$	2-NO_2-4-SO_2CH_3	H	
349	^{i} B $_{u}$	2-NO_2-3-CH_3-4-SO_2CH_3	H	
350	^{i} B $_{u}$	2-SO_2CH_3-5-CH_3	H	

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Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p. (℃)
351	s-Bu	2,4-Cl_2	H	86 - 88
352	s-Bu	2,4-Cl_2	benzyl	oil(NMR-352)
353	s-Bu	2-Cl-4-SO_2CH_3	H	
354	s-Bu	2-Cl-4-SO_2CH_3	benzyl	
355	s-Bu	2-Cl-3-CH_3-4-SO_2CH_3	H	
356	s-Bu	2-Cl-3-CH_3-4-SO_2CH_3	benzyl	
357	s-Bu	2,4-Cl_2-3-CH_3	H	
358	s-Bu	2,4-Cl_2-3-CH_3	benzyl	
359	s-Bu	2-NO_2-4-Cl	H	
360	s-Bu	2-Br-4-SO_2CH_3	H	
361	s-Bu	2-Br-3-CH_3-4-SO_2CH_3	H	
362	s-Bu	2-F-4-SO_2CH_3	H	
363	s-Bu	2-F-3-CH_3-4-SO_2CH_3	H	
364	s-Bu	2-CH_3-4-SO_2CH_3	H	
365	s-Bu	2-Cl-3-Et-4-SO_2CH_3	H	
366	s-Bu	2,3-$(CH_3)_2$-4-SO_2CH_3	H	
367	s-Bu	2,3-Cl_2-4-SO_2CH_3	H	
368	s-Bu	2-CN-4-SO_2CH_3	H	
369	s-Bu	2-CN-3-CH_3-4-SO_2CH_3	H	
370	s-Bu	2-I-4-SO_2CH_3	H	
371	s-Bu	2-I-3-CH_3-4-SO_2CH_3	H	
372	s-Bu	2-Cl-4-SO_2Et	H	

Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p. (℃)
373	^{s}Bu	2-Cl-4-$SO_2{}^{i}$Pr	H	
374	^{s}Bu	2-Cl-4-$SO_2{}^{n}$Pr	H	
375	^{s}Bu	2,4-Cl_2	2,4-chloro-benzoyl	139 - 141.5
376	^{s}Bu	2-NO_2-4-SO_2CH_3	H	
377	^{s}Bu	2-NO_2-3-CH_3-4-SO_2CH_3	H	
378	^{s}Bu	2-SO_2CH_3-5-CH_3	H	
379	Et	2-CF_3-4-SO_2CH_3	H	
380	Et	2-CF_3-4-SO_2CH_3	benzyl	
381	Et	2-CF_3-4-SO_2CH_3	tosyl	
382	Et	2-CF_3-4-SO_2CH_3	phenacyl	
383	Et	2-CF_3-4-SO_2CH_3	mesyl	
384	Et	2-CF_3-4-SO_2CH_3	benzoyl	
385	Et	2-CF_3-4-SO_2CH_3	allyl	
386	Et	2-CF_3-4-SO_2CH_3	propargyl	
387	Et	2-CF_3-4-SO_2CH_3	methyl	
388	Et	2-CF_3-3-CH_3-4-SO_2CH_3	H	
389	Et	2-CF_3-3-CH_3-4-SO_2CH_3	benzyl	
390	Et	2-CF_3-3-CH_3-4-SO_2CH_3	tesyl	
391	^{i}Pr	2-CF_3-4-SO_2CH_3	H	
392	^{i}Pr	2-CF_3-4-SO_2CH_3	benzyl	
393	^{i}Pr	2-CF_3-4-SO_2CH_3	tosyl	
394	^{i}Pr	2-CF_3-4-SO_2CH_3	phenacyl	

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Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p. (℃)
395	^{i}Pr	2-CF_3-4-SO_2CH_3	mesyl	
396	^{i}Pr	2-CF_3-4-SO_2CH_3	benzoyl	
397	^{i}Pr	2-CF_3-4-SO_2CH_3	allyl	
398	^{i}Pr	2-CF_3-4-SO_2CH_3	propargyl	
399	^{i}Pr	2-CF_3-4-SO_2CH_3	methyl	
400	^{i}Pr	2-CF_3-3-CH_3-4-SO_2CH_3	H	
401	^{i}Pr	2-CF_3-3-CH_3-4-SO_2CH_3	benzyl	
402	^{i}Pr	2-CF_3-3-CH_3-4-SO_2CH_3	tesyl	
403	^{n}Pr	2-CF_3-4-SO_2CH_3	H	
404	^{n}Pr	2-CF_3-3-CH_3-4-SO_2CH_3	H	
405	^{n}Bu	2-CF_3-4-SO_2CH_3	H	
406	^{n}Bu	2-CF_3-3-CH_3-4-SO_2CH_3	H	
407	^{i}Bu	2-CF_3-4-SO_2CH_3	H	
408	^{i}Bu	2-CF_3-3-CH_3-4-SO_2CH_3	H	
409	^{s}Bu	2-CF_3-4-SO_2CH_3	H	
410	^{s}Bu	2-CF_3-3-CH_3-4-SO_2CH_3	H	
411	allyl	2-CF_3-4-SO_2CH_3	H	
412	allyl	2-CF_3-3-CH_3-4-SO_2CH_3	H	
413	Et	2-SO_2CH_3-5-CH_3	H	
414	^{i}Pr	2-SO_2CH_3-5-CH_3	H	
415	Et	2-Cl-4-SO_2CH_3-5-CH_3	H	142 - 144
416	^{i}Pr	2-Cl-4-SO_2CH_3-5-CH_3	H	180 - 182

Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p. (℃)
417	Et	2-NO_2-4-SO_2CH_3-5-CH_3	H	
418	^iPr	2-NO_2-4-SO_2CH_3-5-CH_3	H	
419	Et	2-Cl-3,5-$(CH_3)_2$-4-SO_2CH_3	H	
420	^iPr	2-Cl-3,5-$(CH_3)_2$-4-SO_2CH_3	H	
421	Et	2-NO_2-3,5-$(CH_3)_2$-4-SO_2CH_3	H	
422	^iPr	2-NO_2-3,5-$(CH_3)_2$-4-SO_2CH_3	H	
423	Et	2-CH_3-4-Cl	H	
424	Et	2-CH_3-4-Cl	benzyl	
425	Et	2-CH_3-4-Cl	tosyl	
426	Et	2-CH_3-4-Cl	phenacyl	
427	^iPr	2-CH_3-4-Cl	H	
428	^iPr	2-CH_3-4-Cl	benzyl	
429	^iPr	2-CH_3-4-Cl	tosyl	
430	^iPr	2-CH_3-4-Cl	phenacyl	
431	Et	2,3-$(CH_3)_2$-4-Cl	H	
432	Et	2,3-$(CH_3)_2$-4-Cl	benzyl	
433	^iPr	2,3-$(CH_3)_2$-4-Cl	H	
434	^iPr	2,3-$(CH_3)_2$-4-Cl	benzyl	
435	Et	2-Cl-4-SO_2CH_3-5-CH_3	benzyl	105 - 106
436	^iPr	2-Cl-4-SO_2CH_3-5-CH_3	benzyl	
437	Et	2-CH_3-3-Cl-4-SO_2CH_3	H	
438	Et	2-CH_3-3-Cl-4-SO_2CH_3	benzyl	

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Table 2 (cont'd)

Compound No.	R	Xn	Q	m.p. (℃)
439	$^{i}P_{r}$	2-CH_3-3-Cl-4-SO_2CH_3	H	
440	$^{i}P_{r}$	2-CH_3-3-Cl-4-SO_2CH_3	benzyl	
441	Et	2-CH_3-3,4-Cl_2	H	
442	Et	2-CH_3-3,4-Cl_2	benzyl	
443	$^{i}P_{r}$	2-CH_3-3,4-Cl_2	H	
444	$^{i}P_{r}$	2-CH_3-3,4-Cl_2	benzyl	
445	Et	2-CH_3-3-Br-4-SO_2CH_3	H	
446	$^{i}P_{r}$	2-CH_3-3-Br-4-SO_2CH_3	H	

(Note) Et= CH_3CH_2, $^{n}B_{u}$ = $CH_3(CH_2)_3$, allyl= CH_2=CH-CH_2-

$^{n}P_{r}$ = $CH_3CH_2CH_2$, $^{i}B_{u}$= $(CH_3)_2CHCH_2$

$^{i}P_{r}$ = $(CH_3)_2CH$, $^{s}B_{u}$= $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}$

^{1}HNMR	δ (ppm) [solvent]
NMR-2	1.19 (3H, t, CH_3), 3.83 (2H, q, $\underline{CH}_2$ CH_3), 5.48 (2H, s, o - CH_2), 7.20 - 7.40 (9H, m) [$CDCl_3$]
NMR-3	4.14 (2H, q, $\underline{CH}_2$ CH_3), 1.48 (3H, t, CH_2 $\underline{CH}_3$), 2.43 (3H, s, $\overline{CH}_3$) [$CDCl_3$]
NMR-7	6.11 (1H, q, CH), 3.80 (2H, q, $\underline{CH}_2$ CH_3), 1.74 (3H, d, $OCH\underline{CH}_3$), 1.15 (3H, t, CH_2 $\underline{CH}_3$), 7.17 - 7.42 (9H, m) [$CDCl_3$]
NMR-8	1.27 (3H, t, CH_3), 3.94 (2H, q, $\underline{CH}_2$ CH_3), 5.62 (2H, s, O - CH_2), 7.1 - 7.6 (8H, m) [$CDCl_3$]
NMR-10	1.17 (3H, t, CH_3), 2.41 (3H, s, CH_3) 3.81 (2H, q, $\underline{CH}_2$ CH_3), 5.53 (2H, s, -OCH_2) 7.0 - 7.5 (8H, m) [$CDCl_3$]
NMR-11	1.41 (3H, t, CH_2 $\underline{CH}_3$), 4.10 (2H, q, $\underline{CH}_2$ CH_3), 5.18 (2H, s, -OCH_2), 5.13 (1H, = CH_2), 5.51 (1H, = CH_2), 7.2 - 7.5 (4H, m) [$CDCl_3$]
NMR-12	1.44 (3H, t, CH_2 $\underline{CH}_3$), 2.54 (1H, t, J= 2Hz, ≡CH) 4.14 (2H, q, $\underline{CH}_2$ CH_3), 5.15 (2H, d, J=2Hz, -$\underline{CH}_2$ C≡CH), 7.2 - 7.5 (4H, m) [$CDCl_3$]
NMR-29	1.20 (3H, t, J= 7Hz, $CH_2\underline{CH}_3$), 2.77 (3H, S, CH_3), 3.08 (3H, s, SO_2CH_3), 3.85 (2H, q, J= 7Hz, $\underline{CH}_2CH_3$), 5.52 (2H, s, -O-CH_2-), 7.15 - 7.35 (7H, m), 8.00 (1H, d) [$CDCl_3$]
NMR-39	1.19 (3H, t, CH_2 $\underline{CH}_3$), 2.47 (3H, s, CH_3), 3.83 (2H, q, $\underline{CH}_2$ CH_3), 5.51 (2H, s, OCH_2), 7.00 - 7.38 (8H, m) [$CDCl_3$]
NMR-41	1.48 (3H, t, CH_2 $\underline{CH}_3$), 2.42 (3H, s, CH_3), 4.22 (2H, q, $\underline{CH}_2$ CH_3), 6.07 (2H, s, OCH_2), 6.91 - 7.88 (8H, m) [$CDCl_3$]
NMR-42	1.23 (3H, t, CH_2 $\underline{CH}_3$), 2.47 (3H, s, CH_3), 3.92 (2H, q, $\underline{CH}_2$ CH_3), 5.62 (2H, s, OCH_2), 7.01 - 7.50 (7H, m) [$CDCl_3$]
NMR-44	1.14 (3H, t, CH_2 $\underline{CH}_3$), 3.79 (2H, q, $\underline{CH}_2$ CH_3), 5.45 (2H, s, OCH_2), 7.22 - 8.01 (9H, m) [$CDCl_3$]

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^{1}HNMR	δ (ppm) (solvent)
NMR-45	1.46 (3H, t, CH_2 $C\underline{H}_3$), 2.43 (3H, s) 4.10 (2H, q, $C\underline{H}_2$ CH_3), 7.28 - 7.98 (8H, m) ($CDCl_3$)
NMR-85	1.22 (3H, t, J = 7Hz, $CH_2C\underline{H}_3$), 2.29 (3H, s, CH_3), 2.66 (3H, s, CH_3), 3.08 (3H, s, SO_2CH_3), 3.89 (2H, q, J = 7Hz, $C\underline{H}_2CH_3$), 5.53 (2H, s,-CH_2O-) 7.20 (1H, s), 7.25 - 7.40 (6H, m), 7.98 (1H, d) ($CDCl_3$)
NMR-131	1.00 (3H, t, J = 7Hz, CH_2 $CH_2C\underline{H}_3$), 1.20 (3H, t, J = 7Hz ,$CH_2C\underline{H}_3$), 1.45 - 2.08 (2H, m, $CH_2C\underline{H}_2CH_3$), 2.94 - 3.20 (2H, m, -SO_2CH_2-), 3.85 (2H, q, J = 7Hz, $C\underline{H}_2CH_3$), 5.51 (2H, s, OCH_2), 7.15 - 7.93 (9H, m) ($CDCl_3$)
NMR-146	1.21 (6H, d, $CH(C\underline{H}_3)_2$), 4.43 (1H, q, q, $C\underline{H}$ $(CH_3)_2$), 5.50 (2H, s, OCH_2) 7.27 - 7.47 (9H, m) ($CDCl_3$)
NMR-194	1.26 (6H, d, J = 7Hz, CH $(C\underline{H}_3)_2$), 2.31 (3H, s, CH_3), 2.68 (3H, s, CH_3), 3.09 (3H, s, SO_2CH_3), 4.48 (1H, q-q, J = 7Hz, $C\underline{H}(CH_3)_2$), 5.53 (2H , s, -O-CH_2-), 7.22 (1H, s), 7.25 - 7.43 (6H, m), 8.01 (1H, d) ($CDCl_3$)
NMR-221	1.23 (6H, d, J=7Hz, $CH(C\underline{H}_3)_2$), 1.33 (6H, d, J=7Hz, $CH(C\underline{H}_3)_2$), 3.22 (1H, q-q, J=7Hz, $C\underline{H}(CH_3)_2$), 4.43 (1H, q-q, J=7Hz, $C\underline{H}(CH_3)_2$), 5.50 (2H, S, O-CH_2), 7.19 - 7.93 (9H, m) ($CDCl_3$)
NMR-232	4.45 (2H, d, $C\underline{H}_2$ CH=CH_2) 5.50 (2H, s, OCH_2) ($CDCl_3$)
NMR-268	0.94 (3H, t, CH_2 CH_2 $C\underline{H}_3$), 1.87 (2H, CH_2 $C\underline{H}_2$ CH_3), 3.97 (2H, t, $C\underline{H}_2$ CH_2 CH_3) 7.13 - 7.50 (4H, m) ($CDCl_3$)
NMR-269	0.79 (3H, t, CH_2 CH_2 $C\underline{H}_3$), 1.65 (2H, CH_2 $C\underline{H}_2$ CH_3), 3.76 (2H, t, $C\underline{H}_2$ CH_2 CH_3), 5.49 (2H, s, OCH_2), 7.23 - 7.42 (9H, m) ($CDCl_3$)
NMR-292	0.81 (3H, t, CH_3), 1.24 (3H, t, CH_3), 1.66 (2H, CH_2 CH_2 CH_3), 2.64 (2H, q, CH_2 CH_3), 3.77 (2H, t, CH_2 CH_2 CH_3), 5.47 (2H, s, OCH_2), 7.0 - 7.6 (8H, m) ($CDCl_3$)
NMR-296	0.95 (3H, t, CH_3), 1.19 - 2.03 (4H, m), 3.99 (2H, t, CH_2 CH_2 CH_2 CH_3), 7.15 - 7.50 (4H, m), 10.8 (1H, s, OH) ($CDCl_3$)

^{1}HNMR	δ (ppm) (solvent)
NMR-297	0.84 (3H, t, CH_3), 1.03 - 1.71 (4H, m), 3.79 (2H, t, $C\underline{H}_2$ CH_2 CH_2 CH_3) 7.25 - 7.45 (9H, m) ($CDCl_3$)
NMR-320	0.85 (3H, t, CH_3), 1.06 - 1.80 (4H, m) 3.88 (2H, t, $C\underline{H}_2$ CH_2 CH_2 CH_3) 7.15 - 7.46 (8H, m) ($CDCl_3$)
NMR-352	0.67 (3H, t, CH_3 $CHCH_2$ $C\underline{H}_3$), 1.18 (3H, d, $C\underline{H}_3$ $CHCH_2$ CH_3), 1.62 (2H, m, CH_3 CH $C\underline{H}_2$ CH_3), 4.17 (1H, t, q, CH_3 $C\underline{H}CH_2$ CH_3) 5.50 (2H, s, OCH_2), 7.1 - 7.7 (9H, m) ($CDCl_3$)

When the compounds according to the present invention are used for a herbicide, they may be applied generally together with suitable carriers such as solid carriers, e.g., clay, talc, bentonite, diatomaceous earth, etc., or liquid carriers, e.g., water, alcohols (methanol, ethanol, etc.), aromatic hydrocarbons (benzene, toluene, xylene, etc.), chlorinated hydrocarbons, ethers, ketones, esters - (ethyl acetate, etc.), acid amides - (dimethylformamide, etc.). It is possible to add, as necessary, surfactants, dispersing agents, suspending agents, penetrating agents, spreaders, stabilizers, etc. to form arbitrary formulations such as emulsifiable concentrate, wettable powder, flowable (Suspension Concentrate), granule, etc. for practical use.

If necessary, the compounds according to the invention may be mixed, during formulation or application, with other herbicides, various insecticides, bacteriocides, plant growth-regulator, cooper ants, etc.

The other herbicides include the compounds described in "Farm Chemicals Handbook" 69th year of publication (1983).

In the following formulation examples, parts are by weight unless otherwise specified.

Formulation Example 1: Emulsifiable concentrate

Compound No. 19 of the present invention 30 parts

xylene 45 parts

Sorpol 2680 ® 10 parts

(a mixture of non-ionic surfactant and anionic surfactant; trade name supplied by Toho Chemical Co., Ltd., Japan)

dimethylformamide 15 parts

The above ingredients are homogeneously blended with one another in suitable device to giv an emulsifiable concentrate. When in use, it is diluted with a suitable amount of water and applied.

Formulation Example 2: Emulsifiable concentrate

Compound No. 77 of the invention 20 parts

xylene 75 parts

Sorpol 2680 ® 5 parts

(a mixture of non-ionic surfactant and anionic surfactant; trade name supplied by Toho Chemical Co., Ltd., Japan)

The above ingredients are homogeneously blended with one another in suitable device to give an emulsifiable concentrate. When in use, it is diluted with a suitable amount of water and applied.

Formulation Example 3: Wettable powder

Compound No. 152 of the invention 50 parts

Zeeklite A ® 46 parts

(kaolin type clay: trade name supplied by Ziecleid Industries Co., Ltd., Japan)

Sorpol 5039 ® 2 parts

(a mixture of non-ionic surfactant and anionic sur-

factant: trade name supplied by Toho Chemical Co., Ltd. Japan)

Carplex ® (coagulation inhibitor) 2 parts

(white carbon: trade name supplied by Shionogi Pharmaceutical Co., Ltd., Japan)

The above ingredients are intimately mixed and ground in appropriate mills and rollers to give wettable powder. When in use, this wettable powder can be diluted with an appropriate amount of water to obtain suspensions of the concentration required and applied.

Formulation Example 4: Wettable powder

Compound 28 of the invention 50 parts

Zeeklite A ® 46 parts

(kaolin type clay: trade name supplied by Ziecleid Industries Co., Ltd., Japan)

Sorpol 5039 ® 2 parts

(a mixture of non-ionic surfactant and anionic surfactant: trade name supplied by Toho Chemical Co., Ltd., Japan)

Carplex ® (coagulation inhibitor) 2 parts

(white carbon: trade name supplied by Shionogi Pharmaceutical Co., Ltd., Japan)

The above ingredients are intimately mixed and ground to give wettable powder. When in use, this wettable powder is diluted with an appropriatre amount of water and applied.

Formulation Example 5: Flowable (Suspension Concentrate)

Compound No. 18 of the invention 25 parts

Agrisol 8-710 ® 10 parts

(non-ionic surfactant: trade name supplied by Kao Atlas Co., ltd. Japan)

Lunox 1000C ® 0.5 part

(anionic surfactant: trade name supplied by Toho Chemical Co., Ltd., Japan)

1% aqueous Rhodopol 20 parts

(thickening agent: trade name supplied by Rhone-Poulenc S.A.

Water 44.5 parts

The above ingredients are homogeneously mixed to give flowable. When in use, this flowable is diluted with an appropriate amount of water and applied.

Formulation Example 6: Flowable (Suspension Concentrate)

Compound No. 80 of the invention 25 parts

Agrisol 8-710 ® 10 parts

(non-ionic surfactant: trade name supplied by Kao Atlas Co., Ltd., Japan)

Lunox 1000C ® 0.5 part

(anionic surfactant: trade name supplied by Toho Chemical Co., Ltd., Japan)

1% aqueous Rhodopol ® 20 parts

(thickening agent: trade name supplied by Rhone-Poulenc S.A.) Water 44.5 parts

The above ingredients are homogenously mixed to give flowable. When in use, this flowable is diluted with an appropriate amount of water and applied.

Formulation Example 7: Granule

Compound No. 2 of the invention 5 parts

bentonite 55 parts

talc 40 parts

After the above ingredients are intimately mixed and ground, a small amount of water is added thereto and the mixture is kneaded well, granulated by means of an extrusion type granulator and dried to give granules.

The herbicidal compositions containing the compounds according to the present invention are applicable to non-cultivation lands such as athletic fields, vacant lands, railroad sides to damage and control a variety of weeds in addition to agricultural and horticultural lands such as farmlands, paddy fields, fruit gardens, etc. The application dosage of the compounds according to the invention may vary d pending upon the place to be applied, ap-

plicati n season, application manner, kind of weeds to be controlled, cultivated crops, etc., and is generally in the range of 0.01 to 10 kg per hectare - (ha).

The herbicidal effectiveness of the compounds according to the present invention will be explained specifically by way of the following test examples.

Biological Examples

Test Example 1: Herbicidal effect test in submerged conditions

After a certain amount of alluvial soil was placed in a Wagner pot of 1/5,000 are (a), water was added thereto to obtain a sub-merged state of 2 cm in water depth through well mixing. Then, seeds of rice (Oryza sativa) and Barnyard grass - (Echinochloa crus-galli), broadleaf-weeds such as Monochoria vaginalis, Lindernia pyxidaria, Rotala indica, etc. and Scirpus juncoides were mixedly sowed in the submerged soil in the Wagner pot, and tubers of Sagittaria pygmaea, Cyperus serotinus and Eleocharis kuroguwai were placed therein. The pot was placed in the hothouse which keeps the temperature from 20 -25°C to grow the plants.

On the 10th day after sowing, which corresponds to a period when rice and weeds were grown at 1 -2 leaf stage, diluted solution of the chemical which was prepared to become predetermined amount of the chemical was added dropwise by means of a measuring pipette to the soil.

Three weeks after the addition of the chemical liquid, herbicidal effects to rice and each weed were evaluated in the following standard of judgement:

Evaluation Standard :

5 -herbicidal rate above 90 % (completely withered)

4 -herbicidal rate 70 -90 %

3 -herbicidal rate 40 -70 %

2 -herbicidal rate 20 -40 %

1 -herbicidal rate 5 -20 %

0 -herbicidal rate below 5 % (practically no efficacy).

The above herbicidal rate was calculated by the following equation based on the weight measured of live plants above soil in the herbicidal-treatment plot and the untreated plot.

$$\text{Herbicidal rate (\%)} = \frac{A - B}{A}$$

x 100 wherein B : weight of live plant above soil in herbicide-treated plot and A : weight of live plant above soil in herbicide-untreated plot.

The results are shown in Table 3.

Test Example 2: Herbicidal effect by soil-treatment

Sterilized diluvial soil was placed in a plastic pot of 1/10000 are (a) in opening area and 10 cm in depth. Then were sown in spot-like corn (Zea mays), barnyardgrass (Echinochloa crus-galli), green foxtail (Setaria viridis), crabgrass (Digitaria ciliaris), cocklebur, (Xanthium strumarium), velvet leaf (Abutilon theophrasti), smartweed (Polygonum nodosum), pigweed (Amaranthus ascendes) and yellow nutsedge (Cyperus esculentus), respectively. After the seeds were covered with the soil about 1.5 cm in depth, a diluted solution containing a predetermined amount of an active ingredient was applied uniformly over the surface of the soil.

The diluted solution was prepared by diluting with water the wettable powder or emulsifiable concentrate in the above formulation examples and applied by menas of a small spray over the whole surface of the soil. Four weeks after the application, herbicidal effect against various weeds was evaluated according to the following evaluation rating. The results are shown in Table 4.

Evaluation rating:

5 ... above 90 % in herbicidal rate (completely withered)

4 ... 70 to 90 % in herbicidal rate

3 ... 40 to 70 % in herbicidal rate

2 ... 20 to 40 % in herbicidal rate

1 ... 5 to 20 % in herbicidal rate

0 ... less than 5 % in herbicidal rate (practically no effective).

The above herbicidal rate was calculated in similar manner with the Test Example 1.

Test Example 3: Phytotoxity test against cultivated plants by foliage-treatment

In a plastic box of 15 cm (length) x 22 cm - (width) x 6 cm (depth) was placed sterilized diluvial soil, and corn was sown. After covering the seeds with the soil about 1.5 cm in depth and corn plant were grown until 2 leaf stage. A diluted solution containing a predetermined amount of an active ingredient was uniformly applied over the top of corn plant. The diluted solution was prepared by diluting with water the wettable powder or mulsifiable concentrate in the above formulation examples, and the resulting diluted solution was applied by means of a small spray over the whole surface of the plant. Three weeks after the application, phytotoxity against the above crops was evaluated according to the following evaluation rating. The results are shown in Table 5.

Evaluation rating:

5 ... crops are almost completely withered.

4 ... remarkable phytotoxity against crops is observed.

3 ... phytotoxity against crops is observed.

2 ... some phytotoxity against crops is observed.

1 ... phytotoxity against crops is scarely observed.

0 ... no phytotoxity against crops is observed.

Table 3

Compound No.	Application dosage (g/a)	Rice (Orgza sativa)	Barnyardgrass (Echinochloa crus-galli)	Monochoria vaginalis	Lindernia procumbens	Rotala indica	Scirpus juncoides	Sagittaira pygmaea	Cyperus serotinus	Eleocharis kurogwai
1	0.25	0	5	5	5	5	5	5	5	5
	0.125	0	5	5	5	5	5	5	5	5
	0.063	0	5	5	5	5	5	5	5	5
2	0.25	0	5	5	5	5	5	5	5	5
	0.125	0	5	5	5	5	5	5	5	5
	0.063	0	5	5	5	5	5	5	5	5
3	0.25	0	5	5	5	5	5	5	5	5
	0.125	0	5	5	5	5	5	5	5	5
	0.063	0	5	5	5	5	5	5	5	5
4	0.25	0	5	5	5	5	5	5	5	5
	0.125	0	5	5	5	5	5	5	5	5
	0.063	0	5	5	5	5	5	5	5	5
8	0.25	0	5	5	5	5	5	5	5	5
	0.125	0	5	5	5	5	5	5	5	5
	0.063	0	5	5	5	5	5	5	5	5
10	0.25	0	5	5	5	5	5	5	5	5
	0.125	0	5	5	5	5	5	5	5	5
	0.063	0	5	5	5	5	5	5	5	5

Table 3 (cont'd)

Compound No.	Application dosage (g/a)	Rice (Orgza sativa)	Barnyardgrass (Echinochloa crus-galli)	Monochoria vaginalis	Lindernia procumbens	Rotala indica	Scirpus juncoides	Sagittaira pygmaea	Cyperus serotinus	Eleocharis kuroguwai
43	0.25	0	5	5	5	5	5	5	5	5
	0.125	0	5	5	5	5	5	5	5	5
	0.063	0	5	5	5	5	5	5	5	5
44	0.25	0	5	5	5	5	5	5	5	5
	0.125	0	5	5	5	5	5	5	5	5
	0.063	0	5	5	5	5	5	5	5	5
45	0.25	0	5	5	5	5	5	5	5	5
	0.125	0	5	5	5	5	5	5	5	5
	0.063	0	5	5	5	5	5	5	5	5
145	0.25	0	5	5	5	5	5	5	5	5
	0.125	0	5	5	5	5	5	5	5	5
	0.063	0	5	5	5	5	5	5	5	5
Comparative compound D	0.25	4	4	4	5	4	5	4	5	4
	0.125	3	3	3	5	4	5	3	4	3
	0.063	2	2	2	4	3	4	2	3	2
Comparative compound E	0.25	2	5	4	5	5	5	4	5	4
	0.125	1	4	3	4	4	4	3	4	3
	0.063	0	3	2	3	3	3	2	4	2

Table 3 (cont'd)

Compound No.	Application dosage (g/a)	Rice (Orgza sativa)	Barnyardgrass (Echinochloa crus-galli)	Monochoria vaginalis	Lindernia procumbens	Rotala indica	Scirpus juncoides	Sagittaira pygmaea	Cyperus serotinus	Eleocharis kuroguwai
Comparative compound F	0.25	3	4	4	5	5	5	4	4	4
	0.125	2	3	3	4	4	4	3	3	3
	0.063	1	2	2	3	4	3	2	2	2
Comparative compound G	0.25	3	4	4	4	5	5	4	4	3
	0.125	2	3	3	3	4	4	3	3	2
	0.063	1	2	2	2	3	3	3	2	1
Comparative compound H	0.25	2	5	4	4	4	5	4	5	3
	0.125	1	4	4	3	3	4	3	4	2
	0.063	0	3	3	2	2	3	3	3	1
Comparative compound I	0.25	2	5	4	4	4	5	4	5	3
	0.125	1	4	3	3	3	4	3	4	2
	0.063	0	3	2	2	2	3	2	3	1
Comparative compound L	0.25	4	4	3	3	3	4	5	4	3
	0.125	3	3	2	2	3	3	4	3	3
	0.063	2	2	1	1	2	2	3	3	2
Comparative compound M	0.25	2	5	3	4	4	4	4	4	3
	0.125	1	4	2	3	3	3	3	3	2
	0.063	0	3	1	2	2	2	3	2	1

Table 3 (cont'd)

Compound No.	Application dosage (g/a)	Rice (Orgza sativa)	Barnyardgrass (Echinochloa crus-galli)	Monochoria vaginalis	Lindernia procumbens	Rotala indica	Scirpus juncoides	Sagittaira pygmaea	Cyperus serotinus	Eleocharis kuroguwai
Comparative compound N	0.25	3	4	3	4	4	4	4	4	3
	0.125	2	3	2	3	3	3	2	3	2
	0.063	1	2	2	2	2	2	2	2	1

Table 4

Compound No.	Application dosage (Kg/ha)	Corn Zea mays)	Barnyardgrass (Echinochloa crus-galli)	Green foxtail (Setaria viridis)	Crabgrass (Digitaria ciliaris)	Pigweed (Amaranthus ascendens)	Smartweed (Polygonum nodosum)	Cocklebur (Xanthium strumarium)	Velvet leaf (Abutilon theophrasti)	Yellow nutsedge (Cyperus esculeutus)
18	0.25	0	5	5	5	5	5	5	5	5
	0.125	0	5	5	5	5	5	5	5	5
	0.063	0	5	5	5	5	5	5	5	5
19	0.25	0	5	5	5	5	5	5	5	5
	0.125	0	5	5	5	5	5	5	5	5
	0.063	0	5	5	5	5	5	5	5	5
20	0.25	0	5	5	5	5	5	5	5	5
	0.125	0	5	5	5	5	5	5	5	5
	0.063	0	5	5	5	5	5	5	5	5
21	0.25	0	5	5	5	5	5	5	5	5
	0.125	0	5	5	5	5	5	5	5	5
	0.063	0	5	5	5	5	5	5	5	5
28	0.25	0	5	5	5	5	5	5	5	5
	0.125	0	5	5	5	5	5	5	5	5
	0.063	0	5	5	5	5	5	5	5	5
41	0.25	0	5	5	5	5	5	5	5	5
	0.125	0	5	5	5	5	5	5	5	5
	0.063	0	5	5	5	5	5	5	5	5

Table 4 (cont'd)

Compound No.	Application dosage (Kg/ha)	Corn (Zea mays)	Barnyardgrass (Echinochloa crus-galli)	Green foxtail (Setaria viridis)	Crabgrass (Digitaria ciliaris)	Pigweed (Amaranthus ascendens)	Smartweed (Polygonum nodosum)	Cocklebur (Xanthium strumarium)	Velvet leaf (Abutilon theophrasti)	Yellow nutsedge (Cyperus esculeutus)
42	0.25	0	5	5	5	5	5	5	5	5
	0.125	0	5	5	5	5	5	5	5	5
	0.063	0	5	5	5	5	5	5	5	5
152	0.25	0	5	5	5	5	5	5	5	5
	0.125	0	5	5	5	5	5	5	5	5
	0.063	0	5	5	5	5	5	5	5	5
Comparative compound A	0.5	0	5	5	5	5	5	5	5	5
	0.25	0	4	4	4	4	4	4	4	4
	0.125	0	3	3	3	4	3	3	4	4
Comparative compound B	0.5	0	4	3	4	4	4	4	4	4
	0.25	0	3	3	3	3	3	3	3	3
	0.125	0	2	2	2	2	2	2	2	2
Comparative compound C	0.5	0	5	4	4	5	5	5	5	4
	0.25	0	3	3	3	3	4	4	4	3
	0.125	0	3	2	2	3	3	2	3	1
Comparative compound J	0.5	1	4	4	5	4	4	4	4	3
	0.25	0	4	3	4	4	4	3	4	4
	0.125	0	3	2	3	3	3	3	3	2

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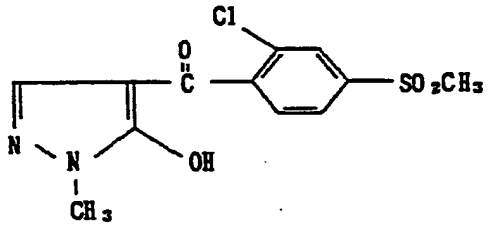
Table 4 (cont'd)

Compound No.	Application dosage (Kg/ha)	Corn (Zea mays)	Barnyardgrass (Echinochloa crus-galli)	Green foxtail (Setaria viridis)	Crabgrass (Digitaria ciliaris)	Pigweed (Amaranthus ascendens)	Smartweed (Polygonum nodosum)	Cocklebur (Xanthium strumarium)	Velvet leaf (Abutilon theophrasti)	Yellow nutsedge (Cyperus esculeutus)
Comparative compound K	0.5	1	4	4	4	4	4	4	4	3
	0.25	0	3	2	4	3	3	3	3	2
	0.125	0	2	1	3	3	2	2	2	1
Atrazine	1.0	1	3	3	2	5	5	5	4	1
	0.5	0	2	2	1	4	4	4	3	0
	0.25	0	1	1	1	4	3	3	2	0

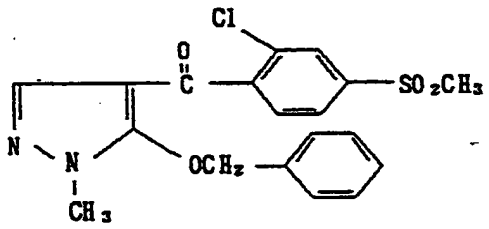
Table 5

Compound No.	Application dosage (Kg/ha)	Corn (Zea mays)
18	2	0
	1	0
19	2	0
	1	0
20	2	0
	1	0
21	2	0
	1	0
28	2	0
	1	0
41	2	0
	1	0
42	2	0
	1	0
152	2	0
	1	0
Comparative compound A	2	2
	1	1
Comparative compound B	2	2
	1	1
Comparative compound C	2	2
	1	1
Comparative compound J	2	3
	1	2
Comparative compound K	2	3
	1	2

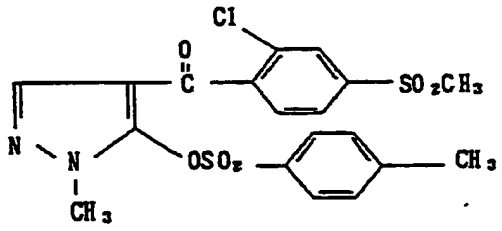
* Comparative Compound A



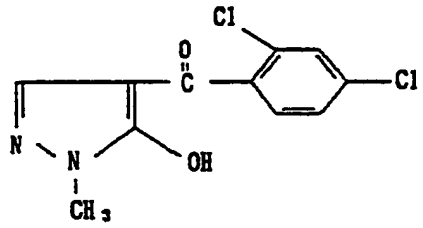
* Comparative Compound B



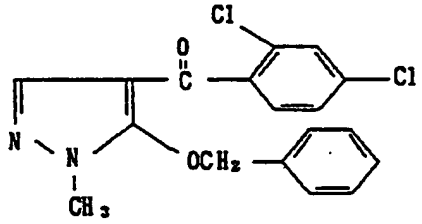
* Comparative Compound C



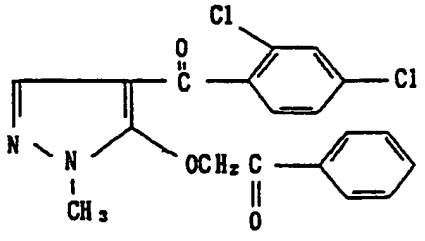
* Comparative Compound D



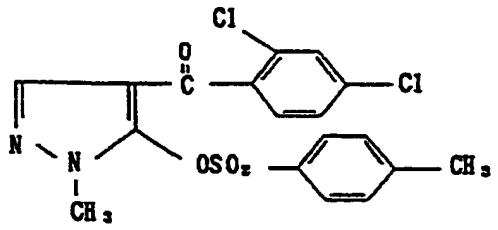
* Comparative Compound E



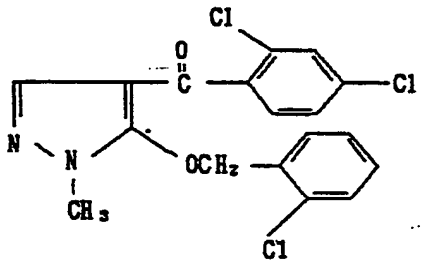
* Comparative Compound F



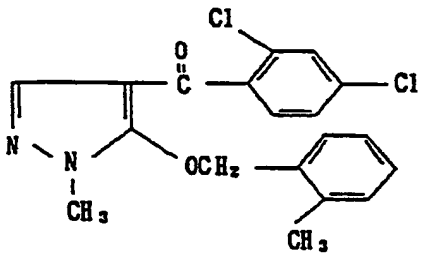
* Comparative Compound G



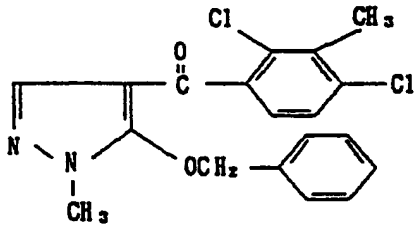
* Comparative Compound H



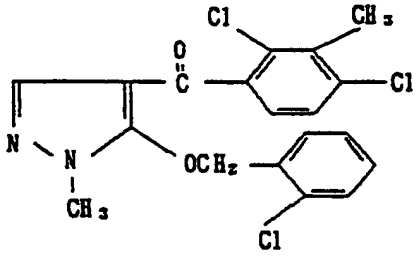
* Comparative Compound I



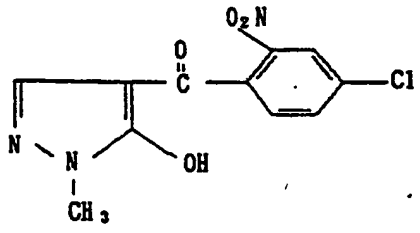
* Comparative Compound J



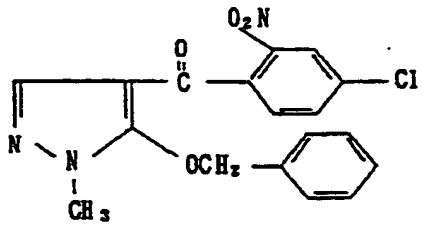
* Comparative Compound K



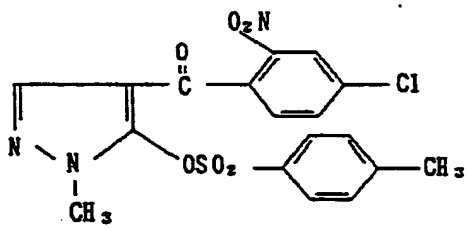
* Comparative Compound L



* Comparative Compound M



* Comparative Compound N



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Claims

1. A pyrazole derivative of the formula I:

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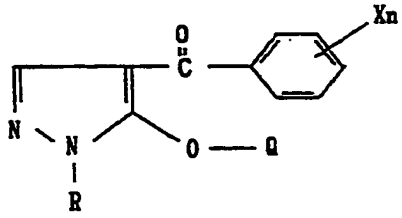


(I)

wherein

R represents an alkyl group having 2 to 4 carbon atoms or an alkenyl group having 2 to 4 carbon atoms which may be substituted by halogen atom,

X represents a halogen atom, a low r alkyl group, nitro group, cyano group, a lower alkylsulfonyl group or trifluoromethyl group,

n represents an integer of 2 to 4,

Q represents hydrogen atom; an aralkyl group which may be substituted by halogen atom, nitro group, cyano group or a lower alkyl group; benzenesulfonyl group which may be substituted by a lower alkyl group r halog n atom; benzoyl group which may be substituted by a lower alkyl group or halogen atom; phenacyl group which may be substituted by a lower alkyl group or halogen atom;

a low r alkyl group which may be substituted by halogen atom;

a lower alkenyl group which may be substituted by halogen atom; or

a lower alkynyl group.

2. A compound of the formula I according to Claim 1, wherein

R represents an alkyl group having 2 to 4 carbon atoms or allyl group,

X represents a halogen atom, a lower alkyl group, nitro group, a lower alkylsulfonyl group or trifluoromethyl group,

n is an integer 2 to 4, and

Q represents benzyl, t syl, methanesulfonyl, benzoyl, phenacyl, allyl, propargyl group or hydrogen atom.

3. A compound of the formula I according to Claim 1, wherein

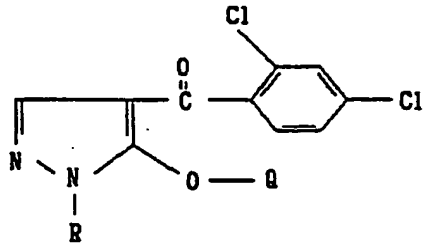
R represents ethyl or isopropyl group,

X represents a halogen atom, a lower alkyl group or methanesulfonyl group,

n is an integer 2 to 4, and

Q represents hydrogen atom, benzyl, tosyl, mesyl, phenacyl, allyl or propargyl group.

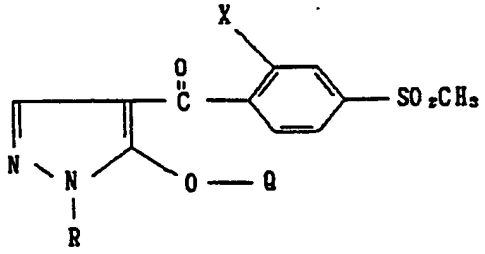
4. A compound according to Claim 1 of the formula V :



(V)

wherein R represents ethyl or isopropyl group, and Q represents hydrogen atom, benzyl or phenacyl group.

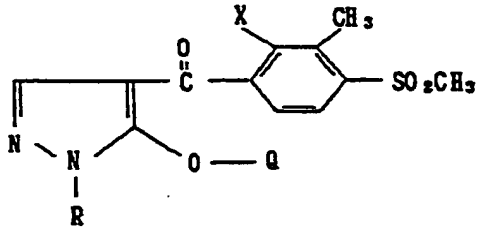
5. A compound according to Claim 1 of the formula VI :



(VI)

wherein R represents ethyl or isopropyl group, X represents methyl group or chlorine atom and Q represents hydrogen atom or benzyl group.

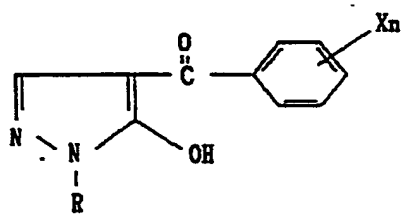
6. A compound according to Claim 1 of the formula VII :



(VII)

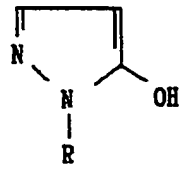
wherein R represents ethyl or isopropyl group, X represents methyl group or chlorine atom and Q represents hydrogen atom or benzyl group.

7. A process for the preparation of a pyrazole derivative of the formula Ia:



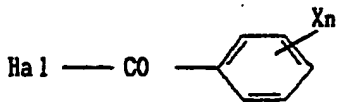
(I a)

wherein R represents an alkyl group having 2 to 4 carbon atoms or an alkenyl group having 2 to 4 carbon atoms which may be substituted by halogen atom, X represents a halogen atom, a lower alkyl group, nitro group, cyano group, a lower alkylsulfonyl group or trifluoromethyl group, n represents an integer of 2 to 4, which comprises c ndensing a compound of the formula II :



(II)

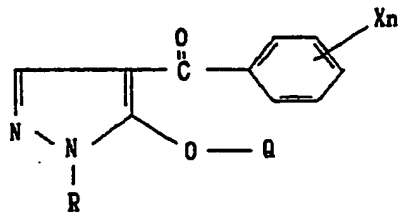
wherein R is as defined above, with a compound of the formula III :



(III)

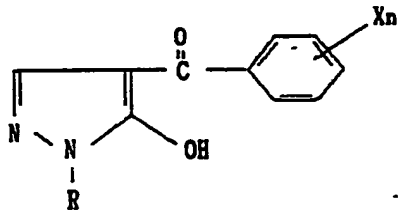
wherein X and n are as defined above and Hal represents a halogen atom, and converting resulting compound to the compound of the formula I.

8. A process for the preparation of a pyrazole derivative of the formula I:



(I)

wherein R represents an alkyl group having 2 to 4 carbon atoms or an alkenyl group having 2 to 4 carbon atoms which may be substituted by halogen atom, X represents a halogen atom, a lower alkyl group, nitro group, cyano group, a lower alkylsulfonyl group or trifluoromethyl group, n represents an integer of 2 to 4, Q represents an aralkyl group which may be substituted by halogen atom, nitro group, cyano group or a lower alkyl group; benzenesulfonyl group which may be substituted by a lower alkyl group or halogen atom; benzoyl group which may be substituted by a lower alkyl group or halogen atom; a phenacyl group which may be substituted by a lower alkyl group or halogen atom; a lower alkyl group which may be substituted by halogen atom; a lower alkenyl group which may be substituted by halogen atom; or a lower alkynyl group, which comprises reacting a compound of the formula Ia:



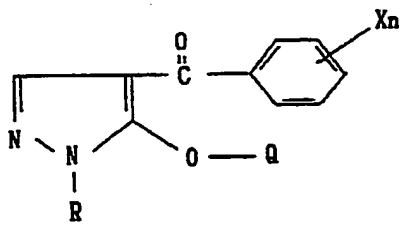
(Ia)

wherein R, X and n are as defined above, with a compound of the formula IV :

Hal ——— Q (IV)

wherein Q is as defin d abov , and Hal represents a halogen atom, to obtain the compound of the formula I.

9. A selective herbicidal composition containing as active ingredient a harbicidally effective am unt of on r more of the compounds of the formula I:



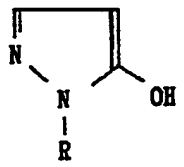
(I)

wherein R represents an alkyl group having 2 to 4 carbon atoms or an alkenyl group having 2 to 4 carbon atoms which may be substituted by halogen atom, X represents a halogen atom, a lower alkyl group, nitro group, cyano group, a lower alkylsulfonyl group or trifluoromethyl group, n represents an integer of 2 to 4, Q represents hydrogen atom; an aralkyl group which may be substituted by halogen atom, nitro group, cyano group or a lower alkyl group; benzenesulfonyl group which may be substituted by a lower alkyl group or halogen atom; benzoyl group which may be substituted a lower alkyl group or halogen atom; a phenacyl group which may be substituted by a lower alkyl group or halogen atom; a lower alkyl group which may be substituted by halogen atom; a lower alkenyl group which may be substituted by halogen atom; or a lower alkynyl group, together with a suitable carriers and/or other adjuvants.

10. The composition according to Claim 9, wherein the compound is one of the compounds claimed in claims 2 to 6.

11. A method for damaging and controlling weeds which comprises applying to the weeds or to the locus thereof a herbicidally effective amount of a compound of the formula I claimed in Claim 1.

12. A pyrazole derivative of the formula II :



(II)

wherein R represents an alkyl group having 2 to 4 carbon atoms or an alkenyl group which may be substituted by halogen atom.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 86 10 6271

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	DE-A-2 513 750 (SANKYO) * Pages 2,3, especially lines 1,2,7 *	1,3-6, 9-11	C 07 D 231/20 A 01 N 43/56
X	AU-B- 515 639 (SANKYO) * Pages 2,3 *	1,3-6, 9-11	
D,A	GB-A-2 122 188 (NISSAN)		

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 07 D 231/00
A 01 N 43/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19-08-1986	DE BUYSER I.A.F.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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